Nitrogen Workshop 2000

Sources, Transformations, Effects and Management of Nitrogen in Freshwater Ecosystems

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Part I: Workshop Report

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Executive summary

THIS REPORT summarises the main conclusions from a specialist workshop on Sources, Transformations, Effects and Management of Nitrogen in Freshwater Ecosystems, held at Monash University on 28–29 March 2000. The workshop was organised by Barry Hart, Mike Grace, Klaus Koop and Richard Davis and sponsored by the National Eutrophication Management Program, the NSW Environment Protection Authority, CSIRO – Land and Water and the CRC for Freshwater Ecology.

The workshop had three objectives:

- collate existing knowledge about the sources, transformations and effects of nitrogen (N) in aquatic systems;
- examine the opportunities for controlling nitrogen through management interventions; and
- identify key knowledge gaps that need to be addressed to make the management interventions viable.

The report first lists six key management questions identified by the workshop. These were used to focus the discussion and conclusions. Then, in Section 3 of the report, we summarise the existing knowledge base regarding the sources, transformations and ultimate effects of nitrogen in triggering and sustaining unwanted algal blooms. Greater detail on each of these three aspects of nitrogen cycling in freshwater systems is provided in the papers prepared by the various specialists.

Section 4 attempts to answer the six key management questions on the basis of the best available scientific knowledge, and to identify where this knowledge is deficient or missing. Finally, in Section 5 specific recommendations regarding priority R&D to fill the identified gaps are made.

The key questions and a summary of the main recommendations follow.

Question 1: Is nitrogen important in the eutrophication of Australian inland waters, and if so, what are the ecological consequences of excessive nitrogen in Australian inland waters?

Key points

- In freshwater systems, both N and phosphorus (P) may control algal growth, but in almost all cases, the algal biomass (or yield) is controlled by the amount of available P.
- There is now evidence showing that in many freshwater (and estuarine) systems algal growth can become N limited, increasing the risk that cyanobacteria will dominate.
- New methods are now available for measuring N limitation, but these are not being used by resource management agencies.
- The specific ecological effects caused by excessive levels of N (eg. cyanobacteria blooms, excessive growth of macrophytes or benthic micro-algae) will depend upon the particular ecosystem type. Present knowledge is insufficient to predict these effects with any certainty.
- Managers should consider the possibility of managing N in all cases, although the actual N reduction targets will depend upon the particular ecosystem.
- Additionally, N reduction strategies need to be coupled with other natural resource management strategies, and not considered on their own.

R&D recommendations

- Commission a R&D project to develop heirarchical decision tools to predict the ecological consequences of excessive N levels in priority ecosystem types.
- Commission a knowledge exchange project to ensure that the new methods for measuring N limitation are more available to resource management agencies.

Question 2: What are the sources of nitrogen that can best be managed?

Key points

- The major sources of nitrogen are from sewage treatment plants (STPs), stormwater, agricultural activities, forests and the atmosphere.

- Inputs from point sources, such as STPs, are the easiest to manage, although the reduction targets to be achieved can vary depending upon the receiving ecosystem.
- Stormwater sources can contribute high nutrient loads, although management of these sources can be difficult because of their highly pulsed nature. Several best management guidelines for managing stormwater are now available.
- Diffuse agricultural sources of nutrients are very difficult to manage. Methods are available for estimating the relative nutrient loads from the different sources in agricultural catchments. However, these are generally too crude to provide specific advice and, further, do not provide information on the bioavailability of the nutrients.
- Timber plantations and farm forestry activities are expanding rapidly in many Australian states. Nutrient inputs from these sources are poorly known.
- Nitrogen inputs from groundwater, the atmosphere and natural forests (particularly mature mountain ash forests) are the most difficult sources to manage.

R&D recommendations

- Commission a critical review of the relative loads and bioavailability of N from a range of different agricultural sources.
- Commission a critical review of the relative importance of natural forests, forestry activities and commercial tree plantations in contributing N (and P) to catchments.
- Commission a critical review of the effectiveness of the available catchment loading models for estimating N budgets for different catchment types.

Question 3: Are the available management strategies for each of these major sources effective? Do we know enough now to assist managers?

Key points

- There is now sufficient information on best management practices (BMP) for urban sources (STP, stormwater), and these BMP guidelines are generally readily available.
- Nitrogen generation from diffuse agricultural sources is not well quantified, although in a number of situations these can be a large source.
- There is clearly a large amount of knowledge on how best to manage these diffuse nutrient sources, but this needs to be better organised to make it more available for managers.
- In managing N and P, two important differences should be considered: biological methods are the only effective way to remove N, and the fates of N and P are controlled by different processes (P controlled by particle transport, N controlled by hydrological processes and transport pathways).

R&D recommendations

- Commission a knowledge exchange project to draw together currently available knowledge for diffuse nutrient sources and use this to develop best management guidelines. In particular, methods for potentially increasing N removal by increasing hydrologic pathways (eg. passing run-off through wetlands, buffer strips and intact tributary streams) should be reviewed.

Question 4: How well linked are N and P? Can P management strategies adequately address N as well, or do we need to do more? If more can we specify? What are the links between N management and management of other environmental factors?

Key points

- The available evidence suggests that catchment N and P processes are not particularly well linked, although a number of the generally adopted P management techniques can also result in some N removal.
- Three general principles related to N management were identified:
  —biological processes (eg. denitrification, biological uptake) are the most effective in removing N, and these can be enhanced in wetlands, buffer strips and small tributary streams;
  —management strategies aimed at removing N should be linked to other management strategies (eg. salinity, phosphorus, water quality); and
  —the loads of both N and P entering waterways need to be controlled in most systems.

R&D recommendations

- Commission a R&D project to investigate the potential control of algal species composition through manipulation of the N speciation (eg. dissolved inorganic N/dissolved organic N ratio).
- Commission an R&D project to investigate important aspects of denitrification in Australia freshwater systems, this to include: the role of benthic micro-algae (also snags, biofilms and macrophytes) in enhancing N removal; the role of small tributary streams in N removal; and the effectiveness of natural and artificial wetlands in removing N.

Question 5: What nitrogen reduction targets should we be aiming for?

Key points

- The current trend is towards significantly increased N use in Australian agriculture.
- Targets for the levels of N reduction should be based on specific ecological outcomes desired (eg. a low frequency of cyanobacterial blooms).
- This will require information on the likelihood of sufficient N being generated and transported within the catchment, and the ecological consequences caused by the catchment-derived N once it enters a waterbody
- The focus should be on managing N (and P) concentrations to minimise local effects at low flow, with the focus on managing loads to minimise downstream effects (eg. in standing waterbodies and estuaries).
- Several decision support tools are available (eg. AEAM, ecological risk assessment) that could be used to assist managers make decisions on the required N reduction targets.

R&D recommendations

- Commission a R&D project to assess and further develop a suite of decision support tools to assist catchment managers to identify appropriate ecological objectives for priority ecosystems, and to set nutrient reduction targets to achieve these objectives.

Question 6: What are the opportunities for management intervention in the nitrogen cycle?

Key points

- Several management principles were identified that could assist resource managers in minimising the adverse effects of N in freshwater ecosystems.
- Nitrogen management should be approached from a systems or catchment perspective.
- In order to set nutrient management priorities for a catchment, it is necessary to identify the major N (and P) sources, quantify the loads transported (and what time of the year this is contributed) and how much of the load is in bioavailable forms.
- It is good management practice to manage nutrients as close to the source as possible, and as far as is possible within the catchment (management becomes more difficult once nutrients enter a waterway).
- There may be scope to reduce losses from N fertilisers by developing cost-effective, slow release N fertilisers; slow release P fertilisers have been adopted by the farming community in Western Australia with impressive results.
- It is good management practice to protect (and perhaps restore) wetlands, small tributaries and riparian vegetation, as these are likely to be the parts of the catchment where most N reduction occurs.
- The time taken to rehabilitate degraded systems may be quite long (eg. decades), and this needs to be factored into nutrient management plans.

R&D recommendations

- Commission a R&D project to determine how best to restore wetlands and floodplain systems such that N removal processes (wet/dry cycles, denitrification, uptake) are reestablished.
- Commission a R&D project to determine the best methods for measuring the bioavailable forms of N.
- Commission a R&D project to determine the role of intact tributary streams in removing N (by denitrification), and the changes in this process if these tributaries are degraded.
- Commission a review to assess the potential for effective and slow release N fertilisers to be produced.

1 Introduction

THERE HAS been considerable investment over the last 10 years in understanding the role that phosphorus plays in controlling algal and cyanobacterial growth in inland waters. As a result, there is now a good understanding of the sources, transport and sinks for phosphorus in inland waters in Australia. The proceedings of a workshop on *Phosphorus in the Landscape* summarises much of this understanding (Davis et al., 1998).

There is increasing evidence that nitrogen can also be a factor limiting algal growth in inland waters. For example, participants at a National Eutrophication Management Program workshop held at Charles Sturt University in 1997 concluded that nitrogen limited algal biomass about as often as phosphorus did during the spring–summer months in the Murray Darling basin (Robertson, 1999). Overseas, Elser et al. (1990) found in a review of North American lakes that nitrogen was limiting just as often as phosphorus. However, less is known about the nitrogen cycle in aquatic environments and the opportunities for controlling nitrogen are not well established.

To help draw together the current knowledge base on nitrogen in the freshwater environment, a specialist workshop was held at the Cooperative Research Centre (CRC) for Freshwater Ecology, Monash University in March 2000. The workshop involved a group of experts in aspects of nitrogen dynamics together with managers concerned with water quality management. The focus of this workshop was on Australia's freshwater ecosystems but, recognising the limited knowledge base about nitrogen in freshwater systems, several experts in nitrogen dynamics in estuarine and marine systems, where the knowledge base is better developed, were also present.

The objectives of the workshop were to:

- collate existing knowledge about the sources, transformations and effects of nitrogen in aquatic systems;
- examine the opportunities for controlling nitrogen through management interventions; and
- identify key knowledge gaps that need to be addressed to make the management interventions viable.

The workshop program is given in Appendix A, a list of participants in Appendix B, and the detailed presentations addressing the first of the above objectives are collated in Appendix C.

The report first lists six key management questions identified by the workshop. These were used to focus the discussion and conclusions. Then in Section 3 of the report we summarise the existing knowledge base regarding the sources, transformations and ultimate effects of nitrogen in triggering and sustaining unwanted algal blooms. Greater detail on each of these three aspects of nitrogen cycling in freshwater systems is provided by the detailed papers prepared by the various specialists. Section 4 attempts to answer the six key management questions on the basis of the best available scientific knowledge, and to identify where this knowledge is deficient or missing. Finally, in Section 5 specific recommendations regarding priority R&D to fill the identified gaps are made.

2 Management issues

KEY MANAGEMENT issues relating to nitrogen management were identified by the workshop (see Table 1). These were then used to focus the subsequent discussion on the current knowledge base, and how this knowledge might be used to assist managers to intervene to reduce the adverse effects of nitrogen in Australian freshwater ecosystems.

From this list of management needs (Table 1), the workshop identified six key questions that needed to be answered.

Question 1: *Is nitrogen important in the eutrophication of Australian inland waters, and if so, what are the ecological consequences of excessive N in Australian inland waters?*

Question 2: *What are the sources of nitrogen that can best be managed?*

Question 3: *Are the available management strategies for each of these major sources effective? Do we know enough now to assist managers?*

Question 4: *How well linked are N and P? Can P management strategies adequately address N as well or do we need specific approaches for N? If specific approaches are needed, can we specify these? What are the links between N management and management of other environmental factors?*

Question 5: *What nitrogen reduction targets should we be aiming for?*

Question 6: *What are the opportunities for management intervention in the nitrogen cycle?*

The workshops recommendations in relation to these key questions are provided in Section 5 – Summary.

Table 1. Management issues related to nitrogen in the freshwater environment

High priority

- How important is N in controlling ecosystem function and should we now be concentrating on N management as well as P management? And what is the relative importance of managing N versus P? Many BGA can fix N, therefore why try to manage N inputs?
- What is the relative importance of the various N sources and loads, and how do we best measure these? And what are the most cost-effective management options for each of the major sources? Cost of N reduction for STP's is high, what level should be aimed for?
- What N targets should be adopted and how should they be developed (ie. how much reduction is needed)? What is the relevance with existing nutrient guidelines and compliance with these?
- Groundwater – How important is N pollution of groundwaters? How important are N-enriched groundwater inputs to wetlands and rivers in stimulating eutrophication?
- Will the adoption of adaptive management strategies assist in N management (ie. do, measure, alter, etc). Can 'assimilative capacity' or 'carrying capacity' be used as a management tool?
- Does ecological risk assessment have a place in better assessing the options for N management in catchments? Is it possible to develop knowledge 'packages' that can assist management agencies in ranking issues?
- For systems that are little impacted now, is it possible to develop guidelines that will ensure N problems do not occur (ie. be proactive rather than reactive)
- How effective is P and TSS management in controlling N? Do we need to do more, and if so what?
- Is it possible to develop management tools for calculating/estimating N budgets taking account of rates of transport and fluxes between N stores?

Continued on next page.

Table 1 (Cont'd) Management issues related to nitrogen in the freshwater environment

High priority (cont'd)

- How do we get better uptake of Best Management Practices?
- How can we get more supportive information packages on N management & how can we improve the use of this information? How best to transfer relevant information on one system to another? Can we achieve better linkages between agricultural and environmental research efforts?

Lower priority

- Major N inputs occur during high flow events – is it possible to manage these pulsed inputs? And should we be targeting different management techniques for wet and dry periods?
- How important are atmospheric inputs of N and what can we do to manage these?
- Need to better understand N transport and transformation processes.
- Is it possible to enhance nitrification and denitrification processes as a means of removing N?
- Is it possible to develop assessment tools for assessing when (and the types of) changes in land use are significant re eutrophication?

3 Knowledge base

3.1 Nitrogen biogeochemical cycle

Nitrogen is an essential element and can exist in aquatic systems in a number of forms. The most important of these are nitrate, ammonium, dissolved organic nitrogen, particulate organic nitrogen, and organic matter making up animals and plants. Nitrate and ammonium are the forms most available for algal growth.

A number of microbial processes exist that can transform many of these forms of nitrogen (Figure 1 illustrates the major processes involved in the biogeochemical cycling of nitrogen in a waterbody) (Fenchel et al., 1998; Harris, 1999). Almost all these transformation processes can occur only with the help of bacteria. For example, organic forms of nitrogen can be decomposed by bacteria to ammonium, which in turn can be converted into nitrate ions in a two step process.

Denitrification, the process by which nitrate is converted to nitrogen gas, is the main way in which nitrogen is lost from aquatic systems. Denitrification predominantly occurs in the sediments.

Certain organisms (eg. N-fixing cyanobacteria) have the capacity to convert atmospheric nitrogen gas into organic nitrogen compounds. This process is known as nitrogen-fixation.

Nitrogen transformation processes have been well studied in estuaries, both overseas and in Australian. In general, estuaries have been the focus of more research than

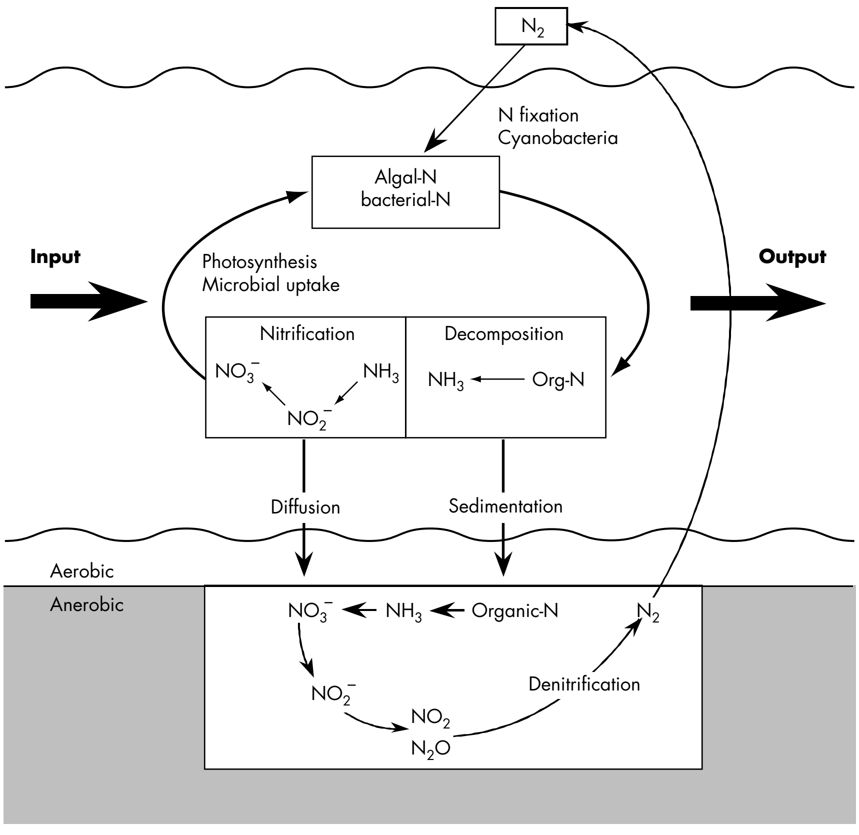

Figure 1. Nitrogen biogechemical cycle showing the range of transformation processes occurring in both the water column and sediments

freshwaters, because they often have major population centres built around them and they are the receivers of land-based contaminants. Major Australian estuaries and coastal regions that have been well studied include Port Phillip Bay (Harris et al., 1996; Murray & Parslow, 1999), Moreton Bay, Swan-Canning Estuary (Hamilton & Turner, 2000), Peel-Harvey Estuary (Humphries & Robinson, 1995), Wilson's Inlet, Hawkesbury River, Richmond River estuary (Eyre & Twigg, 1997), and the Great Barrier Reef (Furnas et al., 1997).

Five findings of relevance to freshwater systems emerge from these studies:

- nitrogen inputs from the catchment are very important, as nitrogen is believed to be the limiting nutrient in these estuarine systems;
- a detailed understanding of the cycling of nitrogen can be obtained only by taking a systems approach, in particular by considering the nitrogen cycle together with other related biogeochemical cycles (eg. carbon, phosphorus, iron) (Harris, 1999);
- nitrogen fixation by cyanobacteria can be an important source of nitrogen to estuarine systems (eg. Peel-Harvey; Robson, 2000);
- denitrification is an important mechanism by which nitrogen is lost from these systems (Heggie et al., 1999);
- benthic algae (microphytobenthos) are an important, but until recently neglected, functional community in most estuaries (Harris et al., 1996).

3.2 Sources

Nitrogen can enter freshwater ecosystems from a wide range of external sources, although not all of these are amenable to management interventions. A characteristic of many of these inputs (as with phosphorus and suspended sediments) is that they are extremely variable and highly dependent upon climatic conditions. The fact that most sources of nitrogen result in highly pulsed inputs to waterbodies has major implications for the management of nitrogen as is discussed more fully below.

Sewage effluents

Sewage discharges, even when well treated, can introduce large concentrations and loads of nitrogen to receiving waters. Depending upon the type of treatment, the main forms of nitrogen will be organic-N, ammonia and nitrate. Almost all sewage discharges in Australia are now licensed, and this has resulted in a considerable decrease in the nitrogen (and phosphorus) loads from this source over the past 20 years. For example, over the 11-year period 1988–89 to 1998–99, the loads of total-N discharged to the Hawkesbury–Nepean River from Sydney Water's sewage treatment plants decreased by almost 50% (3100 kg/d to 1700 kg/d); the reduction in total-P loads was even more significant (240 kg/d to 55 kg/d) (Bickford & Johnstone, this volume).

However, there is still controversy in a number of locations about the level of N removal that should be required; notably the effect of Canberra's effluent on Burrinjuck Reservoir, and the effect of sewage effluent on the Hawkesbury–Nepean River, Sydney. The hypothesis is that if nitrogen concentrations are reduced too much, the N:P ratio in the receiving water may favour the dominance of N-fixing cyanobacteria. As discussed in Section 3.4, nutrients are an important consideration in determining whether unwanted algal blooms occur, but are certainly not the only factor. Thus, consideration of the optimum level of treatment for a particular sewage effluent must involve a detailed consideration of the characteristics of the receiving environment.

Another important source of N to both surface run-off and groundwater is septic tanks, which are used for wastewater treatment in both rural and urban fringe areas. The relative importance of this source is poorly known in most locations (Breen, this volume).

Stormwater

Stormwater inputs can also be very important sources of N (often producing impacts comparable to sewage effluents), and the fact that they are pulsed inputs makes management difficult (ARMCANZ/ANZECC, 1996). The composition of stormwater can vary depending upon the type of contributing (urban) area and the number of (illegal) cross connections to effluent systems (Breen, this volume). Although considerable amounts of water quality data exist for urban streams, it is generally biased to low flows. Very little Australian water quality data exists for direct run-off from urban catchments with particular land uses and known infrastructure quality. Consequently, while urban stream water quality can be described, specific sources responsible for degradation are poorly documented.

There is now a national stormwater management strategy (ARMCANZ/ANZECC, 1996), and a number of Australian States have developed best-management practice guidelines for urban stormwater (BCC, 1999; Victorian Stormwater Committee, 1999). Wong et al. (1999, 2000) have also produced very useful reports on managing stormwater using constructed wetlands and on design options for improving stormwater quality from road run-off.

The ecological effects of urban stormwater are poorly understood, although recent work by Walsh and Breen (Walsh, 2000; Walsh et al., 2000; Breen et al., 2000a) has led to a useful hypothesis that identifies three key factors as having the greatest influence on urban stream 'health', these being water quality, the amount of impervious surface in the catchment and the nature of the drainage system connecting the impervious area to the receiving water (eg. natural channel versus engineered channel versus pipes). The directness and efficiency of the drainage system influences both hydrology and water quality.

Agricultural sources

The use of nitrogenous fertiliser in Australia has increased over the past 40 years (by over 20-fold to around 600,000 t per year by 1995 (Hunter, this volume). Most of this use occurs in cropping areas, although there is significant use of N on non-leguminous pastures in some regions. The major forms of N are ammonium phosphate (47%), urea (43%) and ammonia (6%). Additionally, organic wastes (eg. sewage effluents and biosolids, feedlot wastes) are being increasingly used as fertiliser, although the amounts are less well quantified.

There are few long-term water quality data sets to show whether this increased use of nitrogenous fertilisers has resulted in increased N concentrations in streams and wetlands. Estimates (modelled) for the Johnstone catchment in north Queensland suggest that changes in land use from rainforest to agriculture have increased the nitrate loads five-fold; sugarcane growing areas were found to contribute almost 50% of the nitrate exported (Hunter, this volume).

Irrigation drainage water can contain high nutrient concentrations, although this depends on a range of factors including soil type, fertiliser and water management practices, and crop type (in some situations septic tanks and town stormwater systems can also contribute) (Harrison, 1994; Roberts et al., 1998) and the measured high temporal variations in N concentrations may be explained by differing relative contributions from these sources/activities. In the Goulburn-Broken irrigation system in Victoria, median total-N concentrations are 1.1–2.4 mg L^{-1} (total-P 0.3–0.6 mg L^{-1}) and export rates are around 3.0 kg N $ha^{-1}y^{-1}$ for total-N (total-P 0.8 kg P $ha^{-1}y^{-1}$) (Feehan, this volume). Irrigation drainage water contributes an estimated 21% of the total-N load (total 2880 t y^{-1}) in the Goulburn–Broken catchment (Feehan, this volume). Work in the Johnstone catchment in the wet tropics (Hunter, this volume) showed that the N export rate from areas relying on septic systems was far higher (ca. 70 kg ha^{-1} y^{-1}) than from any other land use (eg. sugarcane & banana areas ca. 40 kg ha^{-1} y^{-1} and other activities less than 20 kg ha^{-1} y^{-1}).

The N-concentrations in the Goulburn–Broken irrigation system are high because the types of irrigated agriculture require high and repeated fertiliser use, with large amounts being exported in drainage water through run-off and possibly leaching. Similar high concentrations are also observed in the Murrumbidgee Irrigation Area (MIA), particularly in regions growing 'summer' crops and row crops (Roberts, pers. comm.). However, in other regions of the MIA (and southern NSW), where rice is (has been) the dominant crop in irrigation, drainage waters do not necessarily have such high concentrations of nitrogen.

The contribution from *dryland agricultural* sources of N is obviously dependent upon rainfall to transport the N to waterways, and thus the inputs of N from these sources will be highly pulsed with large bursts occurring during high flow periods. This pulsed nature of the inputs makes management difficult.

Depending upon the mix of agricultural activities in the catchment, the major sources of N may be quite different to the P sources. For example, in the Goulburn–Broken catchment, dryland areas are the most significant sources of N (estimated 65% of the total annual load, much greater than the inputs from irrigation areas), with atmospheric and natural forest sources being very important contributors, while the irrigation areas are the major sources of P (total-P load—370 t y^{-1}; irrigation drains 47%, dryland 30%; Feehan, this volume).

Overseas research suggests that the planting of riparian buffer strips along headwater and tributary streams can be an important way to reduce nutrient inputs. Studies have been conducted showing the effectiveness of such buffer strips for reducing the inputs of both nitrogen and phosphorus. Unfortunately, there is little detailed knowledge of how efficient these buffer strips are for trapping N in Australian systems, although research being carried out by the CRC for Catchment Hydrology will provide some important information on this aspect.

Forest sources

It is well known that some mature native forests (eg. old growth mountain ash) leak relatively high concentrations of nitrate (Attiwill et al., 1996). Rainforests also contribute relatively high fluxes of N (eg. ca. 10 kg N $ha^{-1}y^{-1}$—Hunter, this volume). The workshop identified the need for a compilation of typical N fluxes from different forest types in Australia to assist in attributing the relative exports from these sources into context with other catchment sources. However, even with this information, it was recognised that there will be difficulties in managing these sources.

The workshop also noted that there is currently a rapid increase in the number of commercial timber plantations (and farm forestry activities), with almost no information available on the relative propensity of these activities to become major N sources within particular catchments. This aspect needs urgent attention. What is needed is a review of the expected nutrient loads from commercial timber plantations, taking into consideration the different tree species used and the management practices employed, and the identification of best management practice to reduce nutrient run-off.

Atmospheric sources

There is relatively little quantitative information on the relative loads of nitrogen input from the atmosphere (Meyer et al., this volume). The major sources that contribute to atmospheric fixed nitrogen are soil microbial processes, animal excreta, biomass burning, fossil fuel consumption and lightning. The major sink processes returning fixed nitrogen from the atmosphere are wet and dry deposition. Meyer et al. (this volume) estimate that the rate of emission of fixed nitrogen over Australia is of the order of 3 kg N $ha^{-1}y^{-1}$ and the observed deposition rates vary from 0.3 kg N $ha^{-1}y^{-1}$ for oceanic, to 2 kg N $ha^{-1}y^{-1}$ for remote rural areas, to 4 kg N $ha^{-1}y^{-1}$ for rural areas with major coal fired utilities to 11 kg N $ha^{-1}y^{-1}$ for urban regions. There can be major changes in the form of nitrogen emitted to the atmosphere and that subsequently deposited from the atmosphere.

The workshop identified the potential for increased collaboration between atmospheric and freshwater scientists in better quantifying the amounts and possible effects from atmospheric nitrogen.

Groundwater sources

The workshop did not have participants with the expertise to review groundwater sources of nitrogen. However, a number of participants identified nitrogen-rich groundwaters as a potentially important source of nitrogen for wetlands, and for streams under low flow conditions. For example, it was noted that groundwater contributed a significant fraction of the total nutrient load to the Swan–Canning Estuary, in Western Australia (Linderfelt & Turner, 2000).

The workshop also made the distinction between (agriculturally) contaminated groundwater and groundwater containing naturally high nitrogen concentrations. Given the possible links between agriculture and nitrogen pollution of groundwater, this distinction could be very important for the long-term management and sustainability of streams and wetlands receiving such groundwater.

The workshop recommended that a review of groundwater as a source of nitrogen to streams and wetlands be undertaken.

3.3 Transformations

The major in-stream transformation processes involving nitrogen fixation, nitrification and denitrification, are well known (Fenchel et al., 1998; Harris, 1999). These transformations occur in both the water column and in the sediments (see Figure 1).

Nitrogen transformation processes

Nitrogen transformation processes mostly occur in sediments, are largely controlled by microbes and are very dependent upon temperature and redox conditions (Boon; Ford, this volume). It is known that the nitrogen biogeochemical cycle can be coupled to other cycles, particularly the carbon, phosphorus, sulphur and iron cycles (Fenchel et al., 1998; Harris, 1999), and for this reason the workshop stressed the need to take a systems approach when studying nitrogen transformations.

Measurement of the rates of transformation processes, such as nitrification and denitrification, in sediments is difficult because of the heterogeneous nature of sediments in many freshwater systems. However, there are a number of new *in situ* techniques (eg. MIMS—membrane injection mass spectrometry) that should become readily available in the near future, and will result in a considerably improved understanding of the importance of these processes in Australian freshwater systems.

Both heterotrophic and autotrophic bacteria are very important in freshwater systems (Fenchel et al., 1998; Boon, this volume). They have a large N demand (grow fast) and are generally very productive. For example, bacterial secondary production in a tropical coastal system was ca. 10–30% of the primary production of seagrasses and had a similar nitrogen demand (Boon, this volume). The workshop identified the need to consider role of viruses and zooplankton in controlling bacteria (note: in Australian freshwaters the zooplankton are dominated by rotifers not daphnia).

There are some very useful new methods available for studying the bacteria involved in nitrogen transformation in natural systems, in particular using molecular probes (Atlas & Bartha, 1993; Brock & Madigan, 1994), enzyme analysis (Sinsabaugh et al., 1997) and ^{15}N stable isotopes (J.W. Udy & S.E. Bunn, unpublished data; Tank et al., 2000).

The important role of benthic algae and microbial biofilms in modifying nitrification and denitrification processes in estuarine and marine systems has been known for some time (Seitzinger, 1996; Heggie et al., 1999; Murray & Parslow, 1999; Light, this volume). However, it is only recently that evidence for the potential importance of such in-stream biological processes in freshwater systems has also emerged. For example, recent work in the Mississippi River has shown that N losses in streams within the basin were substantial and very important in limiting the extent of eutrophication in the downstream Gulf of Mexico (Alexander et al., 2000).

Interestingly, it was found that the small streams were almost 100 times more effective than the main river in reducing nitrogen.

Current studies in the Yarra and Brisbane rivers will provide a more detailed understanding of the role of benthic algae and biofilms on the nitrification and denitrification processes in Australian streams (S. Bourgues, M. Grace, P. Ford & B.T. Hart, unpublished data; Bunn & Davies, 2000), and will assist in answering questions of importance to managers, namely just how important, in general, are these processes, and can they can be manipulated to manage nitrogen.

Wetlands are depositional areas, often with highly organic sediments and dominated by macrophytes. It is thought that denitrification should be important in these systems because of the close proximity of oxygenated and de-oxygenated zones. Biofilms should also be important in promoting denitrification. However, there have been very few measurements of the rates of key nitrogen transformation processes in wetlands, with most of the available information being related to the size of the nitrogen pools in these systems.

The wetting and drying cycles in wetlands can be important in stimulating nitrogen and phosphorus release (Qiu & McComb, 1996; Baldwin et al., 1997; Baldwin & Mitchell, 2000; Baldwin et al., this volume), but just how this factor can be fitted into the management of these systems needs more consideration.

Measurement of N transformation processes

The rates of the nitrogen transformation processes (and the controlling factors) are not well established for Australian freshwater systems, although there are now several Australian research groups able to measure rates of nitrification, denitrification and nitrogen fixation (Udy, this volume). Much of the present focus in Australian freshwater systems is on denitrification, which is the most important mechanism for reducing nitrogen loads and transport to downstream estuaries. The workshop also considered that nitrogen fixation may be important in some freshwater and coastal lagoon systems, particularly those where N-fixing cyanobacteria are present, and recommended that more information be collected on this aspect.

Considerably more information on the rates of nitrogen transformation in Australian freshwater systems is expected to become available over the next few years.

Modelling

Harris (1998) has commented upon the need for predictive models to assist in managing the spatially and temporally variable freshwater systems in Australia. Predictive computer-based models are available for modelling a number of the nitrogen processes, in particular sediment processes (Blackburn et al., 1994; M. Harper, unpublished data) and algal growth (Hamilton & Schladow, 1997; Flynn & Fasham, 1997; Geider et al., 1988). Given the complexity of the nitrogen cycle, the workshop concluded that modelling will be essential for improving the understanding of various nitrogen processes and for coupling the scientific understanding with best management practice.

For example, simulations reported by Webster (this volume) show that systems with low input rates of organic nitrogen have very low denitrification rates, mainly because there is insufficient dissolved organic carbon to react with the nitrate (organic C limited). Then as the loading rate increases, so does the denitrification rate. But at high loading rates, the denitrification rate again falls because the system has insufficient oxygen available for the nitrification step (nitrate limited). The balance between nitrification and denitrification may have a major influence on the flora (macrophytes, macro-algae, phytoplankton) supported in a particular freshwater system. Coupled transport–sediment–growth models will assist in focusing the on-ground research that will be needed to investigate such an hypothesis.

Transport. Nitrogen loading models can be helpful in providing information on nitrogen budgets and nitrogen transport from various sources within a catchment. For example, models such as AEAM, CMSS, AQUALM and LASCAM have been used in a number of catchments to provide a first approximation of the loads of nitrogen (and phosphorus) entering waterways, and to assist in identifying the relative importance of the various sources (Grayson et al., 1994; Davis & Farley, 1997; Phillips et al., 1992; Viney & Sivapalan, 2000). However, the variable and pulsed nature of these land-based processes in Australian systems has meant that the rates of many of the N processes are still poorly known, and this has limited the application of such models.

The workshop stressed that attention needs to be given to the relevant spatial and temporal scales to ensure that the important processes are adequately modelled. For example, since most nitrogen is transported in solution, processes such as sedimentation that have a major effect on the loads of phosphorus transported, will be much less important for nitrogen.

Sediments. Some relatively simple sediment nutrient models are now available (M. Harper, unpublished data). These are being used to assist in better understanding the microbial processes occurring in sediments (Webster, this volume), to provide information on possible management scenarios, and to assess the time that it will take for effective reductions in algal biomass to occur in systems where in situ nutrient sources are important (M. Harper,

P. Ford, M. Grace, S. Bourgues & B.T. Hart, unpublished data),

Three possible improvements to the present simple models were suggested. The first was the inclusion of a benthic algal component to account for the influence of this factor on the nitrification and denitrification processes. CSIRO has begun some work on this aspect (Webster, this volume). The second was the possible improvement in understanding the nitrification and denitrification processes if the specific bacterial groups (eg. nitrifiers, denitrifiers) were incorporated, rather than using general bacterial processes. A considerable amount of the information required to do this is available in the wastewater treatment literature (Hamilton, this volume). Third was the possible inclusion of macrophytes as nutrient pumps, taking nutrients from depth in the sediments and releasing them to the water column. The relative importance of this mechanism in Australian freshwater systems is poorly known.

Algal growth. Oliver & Ganf (2000) have stressed that the occurrence and abundance of particular species of cyanobacteria is not dependent upon one particular environmental stimulus, but depends upon a complex interplay of factors. They have also produced a useful flow chart (Figure 2) which summarises the key physical, chemical and biological factors, and the interactions between these factors, that control the growth of particular cyanobacterial species.

Others have developed computer models to predict phytoplankton and cyanobacterial growth in freshwater systems (Patterson et al., 1994; Sherman & Webster, 1994; Hamilton & Schladow, 1997; Sherman et al., 1998). These range from simple models incorporating flow, wind and source of water as the major variables, to successfully predict whether cyanobacteria will dominate in the lower River Murray (Brooks et al., this volume), to more complex hydrodynamic and water quality models, such as DYRESM–WQ (Patterson et al., 1994; Hamilton, this volume).

Hamilton (this volume) identified the need for improved understanding of key processes involved in the biogeochemical cycling of nitrogen in aquatic systems, and particularly nitrogen-fixation and benthic primary production, if numerical models with greater predictive capacity are to be developed.

3.4 Effects

The influence of nitrogen forms on aquatic plants was covered in the workshop. Most emphasis was on bloom-forming phytoplankton, such as cyanobacteria (nitrogen-fixing and non-nitrogen fixing species) and micro-algae (Oliver; Brooks et al., this volume). However, benthic micro-algae (microphytobenthos) (Light, this volume) and macrophytes (Roberts, this volume) were also considered.

Nitrogen can be acquired by aquatic plants in three forms—ammonium (NH_4^+), nitrate (NO_3^-) and dinitrogen (N_2). Ammonium is the most preferred, while N_2 can be utilised only by nitrogen-fixing cyanobacteria and even then only after the other preferred sources of nitrogen are exhausted (Oliver & Ganf, 2000).

Phytoplankton

The factors leading to algal blooms in Australian freshwaters have been reviewed by Jones (1994) and Oliver & Ganf (2000). The review by Oliver & Ganf (2000) focused particularly on the conditions that could lead to gas vacuolate cyanobacteria (eg. *Anabaena, Microcystis*), the algal species principally responsible for blooms, dominating over eukaryotic micro-algae. The main factors considered are:

- *regulation of buoyancy*—in deep waters this allows the cyanobacteria to optimise their growth conditions;
- *response to phosphorus concentrations*—there is no evidence that the general response to phosphorus reductions is different between cyanobacteria and micro-algae. There will be a reduction of biomass with a decrease in phosphorus concentration, but the extent and nature of the response is dependent upon the internal phosphorus load and the magnitude of the external load. When the initial P concentrations are in excess of the algal requirements, the effects of P-removal may be minimal, and if internal loads are significant it may take many years for any reduction in biomass to be noticed;
- *TN:TP ratio*—has been used to provide a rough guide to whether nitrogen or phosphorus is limiting in the waterbody (Guildford & Hecky, 2000). The general theory is that if the molar TN:TP ratio is less than about 16, the system is nitrogen limited, and under these conditions nitrogen-fixing cyanobacteria are more likely to dominate. Unfortunately, in many Australian freshwater systems the TN:TP ratio does not accurately reflect the biologically available nitrogen and phosphorus concentrations. A generally accepted paradigm is that freshwater systems are phosphorus limited, while estuarine and coastal systems are nitrogen limited. However, Wood & Oliver (1995) have used both traditional and new methods to show that N-limitation to growth is quite common in many Australian freshwater systems. Unfortunately, the methods used by Wood and Oliver (1995) are still not commonly available to resource management and environmental protection agencies to assess the N sensitivity of receiving waters. The workshop recommended that additional work aimed at making these methods more available should be undertaken;

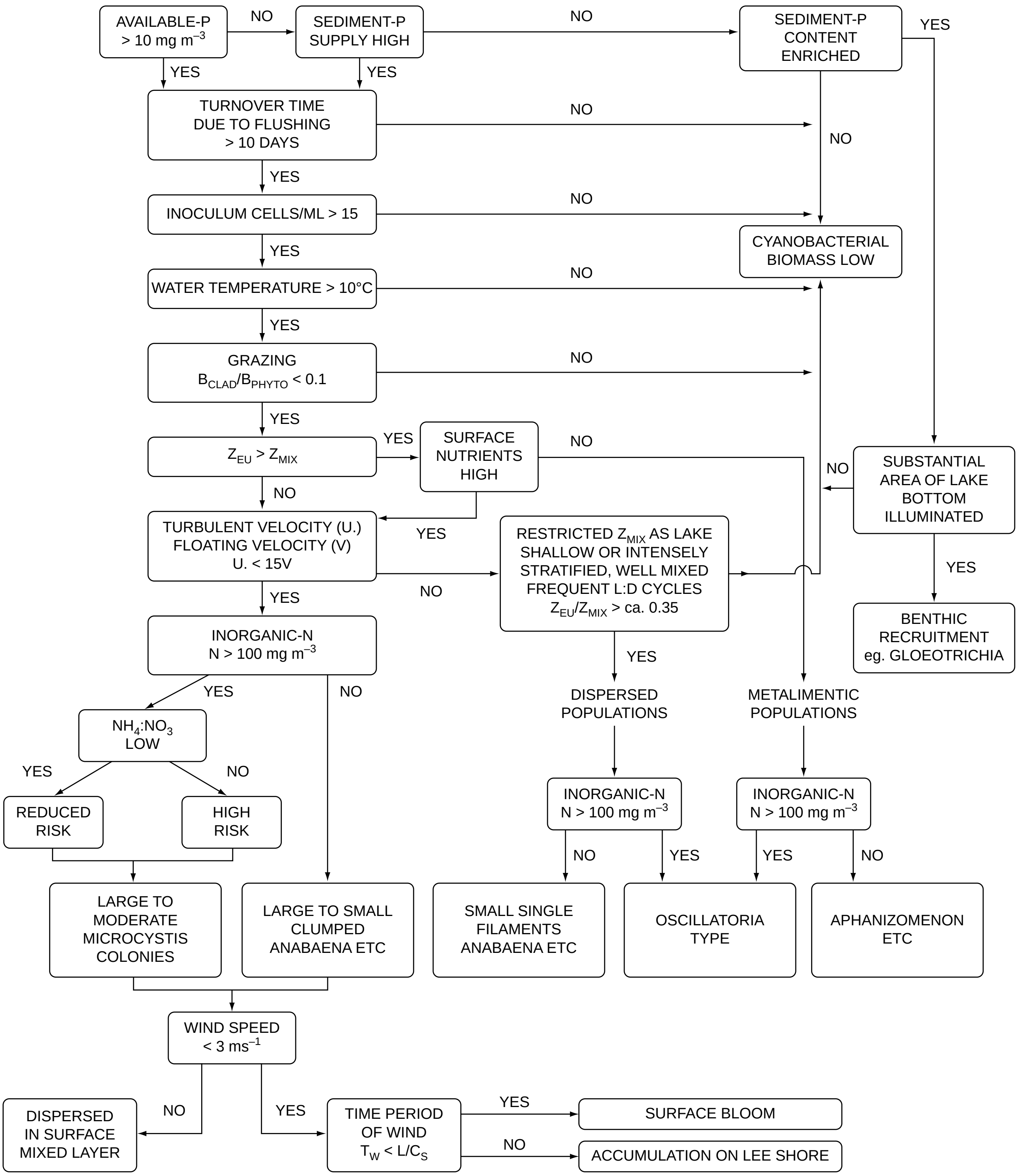

Figure 2. Flow chart summarising the major environmental characteristics supporting the development of cyanobacterial blooms and selecting for particular genera. Key: B_{CLAD} biomass of cladoderms; B_{PHYTO} biomass of phytoplankton; z_{eu} euphotic depth; z_{mix} depth of mixing; V floating or sinking velocity of cyanobacteria; t_w time that the wind blows; L lake fetch; c_s surface current speed

- *form of inorganic nitrogen*—there is evidence suggesting that the form of nitrogen can influence the resulting phytoplankton species composition. It seems that non-nitrogen fixing cyanobacteria are favoured by ammonium, and micro-algae by nitrate. The nitrogen-fixing cyanobacteria are favoured by nitrogen deficiency and are clearly advantaged when the inorganic nitrogen concentration is low (generally below ca. 100 µg N/L), although these populations may ultimately be limited by the available phosphorus concentration;[1]
- *grazing*—it appears that zooplankton grazing can reduce the cyanobacterial biomass provided the zooplankton are present before the cyanobacteria attain a size larger than the animals can manage;
- *hydrodynamics*—water retention time is a key factor determining whether cyanobacterial blooms will occur. Several studies have shown that the occurrence of *Anabaena circinalis* is a function of discharge rate in regulated Australian rivers (Webster et al., 1996; Baker et al., 2000; Brooks et al., this volume). Sherman et al. (1998) found that when flows in Maude Weir on the Murrumbidgee River were between 500 and 1000 ML/d, the population density of the diatom *Aulacoseira (Melosira) granulata* decreased while *Anabaena circinalis* increased. They attributed this shift in species composition to thermal stratification which leads to a favourable environment for buoyant species such as *Anabaena;*

Oliver & Ganf (2000) concluded that “the occurrence and abundance of various types of gas-vacuolate cyanobacteria is not reliant on any one particular environmental stimulus, but depends on a complex interplay of factors”. They provided a decision tree that can be used by managers to identify the likely key factors for any one particular system (Figure 2).

These findings have important implications for the management of nutrients in Australia freshwaters. The workshop stressed three points. First, nutrient management plans need to ensure that, in managing nitrogen, the nitrogen concentrations are not reduced to such a level that nitrogen-fixing cyanobacteria are preferentially selected over other more preferred algal species (eg. diatoms). Second, even in those systems where nitrogen is the nutrient limiting immediate algal growth (limiting nutrient), phosphorus will be the nutrient more commonly limiting the ultimate biomass (Figure 3). Thus, phosphorus reduction should still be the primary aim of nutrient management plans. And third, the complexity of the nitrogen cycle will always make nitrogen management difficult, although there are opportunities, through denitrification, ammonia volatilisation and biological uptake, to manipulate and manage nitrogen inputs to waterways (at least for relatively small inflows).

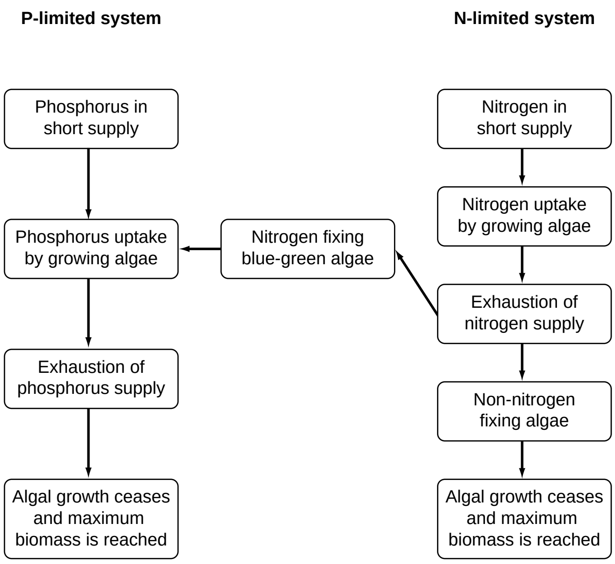

Figure 3. Processes occurring in N-limited and P-limited aquatic systems, showing the likely change-over to nitrogen-fixing cyanobacteria in an N-limited system

Benthic micro-algae

Several recent studies, mainly in estuarine regions of Australia, have noted the importance and complexity of benthic micro-algal communities (Heggie et al., 1999; Murray & Parslow, 1999). These estuarine benthic micro-algae can be major primary producers (often comparable to or greater than phytoplankton on an areal basis) and fixers of nitrogen, and at least in Port Phillip Bay, are vital in sustaining nitrification and denitrification. The importance of these communities in freshwater systems is presently unknown, but the small amount of work emerging suggests they may be equally important in some freshwater ecosystems (Light, this volume; Breen et al., 2000b; Bunn & Davies, 2000; M. Grace, P. Ford, S. Bourgues and B.T. Hart, unpublished data).

The workshop recommended that benthic micro-algae be considered as an integral component in models of nitrogen biogeochemical cycling. The challenge will be to obtain better knowledge of exactly where and when benthic algae are important in Australian freshwater systems. Such research will require strong collaboration between the various disciplines. When this basic knowledge about benthic micro-algal communities is available, managers will be better able to maintain and perhaps enhance habitats critical for benthic algae.

1. The Workshop noted that there are few (if any) measurements of nitrogen-fixation by cyanobacteria in Australian freshwaters, and that this deficiency in information should be redressed.

Macrophytes

Large aquatic plants or macrophytes are a diverse group of organisms, with emergent, submerged, floating and rooted species all being present in Australian freshwater systems. Available overseas information suggests that the different macrophytes respond differently to nitrogen enrichment, although there have been very few Australian studies on the interactions between N-enrichment and macrophyte growth (Roberts, this volume).

Perhaps the most important role of macrophytes in the nitrogen cycle is as 'facilitators' of other processes (Roberts, this volume). They can modify the sediment environment, for example through rhizome oxygen exchange with the surrounding sediment, which has implications for nitrification and denitrification processes, and also provide a substrate for epiphytes and biofilms which may enhance the occurrence of nitrogen-fixation and also nitrification and denitrification. The workshop also identified the potential for macrophyte canopy tissue N:P ratios to be used as a screening tool for assessing the bioavailable in-sediment nutrient condition of a site (Roberts, this volume).

4 Summary

Question 1: Is nitrogen important in the eutrophication of Australian inland waters, and if so, what are the ecological consequences of excessive nitrogen in Australian inland waters?

The workshop concluded on the basis of the available evidence that excessive nitrogen was a very important factor in reducing the ecological functioning of many Australian inland waters, mostly through eutrophication of the resource. As with most resource management issues, the adverse effects of excess nitrogen are highly dependent upon a range of other factors (eg. flow conditions, phosphorus concentration, grazing pressures, light climate), and may be ecosystem specific.

There is now sufficient evidence to seriously challenge the paradigm that freshwater systems are primarily phosphorus limited. As discussed above, it has now been shown that N-limitation on growth commonly occurs in many Australian freshwater systems. The workshop recommended that additional work aimed at making the new N-limitation measurement methods more available to resource management agencies, should be undertaken.

For many coastal catchments, the workshop also identified that, in addition to possible eutrophic effects in waterbodies within the catchments, there was also the very real possibility of eutrophication problems due to excessive nitrogen in the downstream estuarine and coastal systems.

The workshop concluded that the possibility of managing nitrogen should be considered in all cases, but that the actual nitrogen reduction targets to be achieved will depend on the system being managed. Additionally, nitrogen reduction strategies need to be coupled with other natural resource management strategies and not considered on their own.

The workshop identified a lack of detailed information on the specific ecological effects caused by excessive levels of nitrogen (eg. cyanobacteria blooms, excessive growth of macrophytes or benthic micro-algae), and recommended that this be a focus of an R&D project.

KEY POINTS

- In freshwater systems, both N and P may control algal growth, but in almost all cases, the algal biomass (or yield) is controlled by the amount of available P.
- There is now evidence showing that in many freshwater (and estuarine) systems algal growth can become N limited, increasing the risk that cyanobacteria will dominate.
- New methods are now available for measuring N limitation, but these are not being used by resource management agencies.
- The specific ecological effects caused by excessive levels of N (eg. cyanobacteria blooms, excessive growth of macrophytes or benthic micro-algae) will depend upon the particular ecosystem type. Present knowledge is insufficient to predict these effects with any certainty.
- Managers should consider the possibility of managing N in all cases, although the actual N reduction targets will depend upon the particular ecosystem.
- Additionally, N reduction strategies need to be coupled with other natural resource management strategies, and not considered on their own.

Question 2: What are the sources of nitrogen that can best be managed?

The workshop identified the following major nitrogen sources: sewage treatment plants (STPs), stormwater, agriculture, forests and the atmosphere. Many of these sources can and are being managed in specific catchments. However, there is still a general lack of information for most catchments on the relative importance of the different sources.

Several methods are currently being used around Australia to estimate the relative loads of nitrogen (and phosphorus) generated by different activities and land uses. For example, AEAM (Grayson et al., 1994), CMSS (Davis & Farley, 1997), catchment loading model (Phillips et al., 1992), statistical techniques (Donohue et al., 2000) and LASCAM (Viney & Sivapalan, 2000) have all been used. Such loading estimates are extremely useful in determining the priorities for management, but are far too crude to provide specific advice. A deficiency noted with most of these estimation methods is that the uncertainties or errors in the calculations are not included, and they are generally not able to provide in formation on the bioavailability of the nutrients being transported; the latter being a result of the lack of detailed information on nitrogen cycling processes in these models. There is an urgent need for models which incorporate such detailed process understanding.

Monitoring programs to quantify loads from sources such as STPs and stormwater are relatively well developed, although the application of event sampling for stormwater loads is not always done well. The workshop identified the potential importance of septic tanks as a source of nitrogen, but reported that there is a general lack of information on the relative importance of this source in most catchments.

Nitrogen inputs from groundwater, the atmosphere and natural forests (particularly mature mountain ash forests), were identified as the most difficult sources to manage.

The workshop also identified the current development of timber plantations and farm forestry as an activity that could result in increased nitrogen loads in some catchments (Hart, 2000). Information is needed on the relative importance of natural forests, forestry activities and commercial timber plantations as sources of nitrogen. It is recognised that some of these nitrogen sources, particularly those which go to the groundwater, will be difficult to manage.

The workshop noted a major knowledge gap in the capacity to predict the different forms of nitrogen entering freshwater (and estuarine) systems. The various estimation methods referred to above all provide estimates of total nitrogen. However, it is well known that the different forms of nitrogen (eg. organic-N, nitrate, ammonium), are transported at quite different rates, interact in different biogeochemical reactions, and influence macro-algae and cyanobacteria differently. For example, the bioavailability of the nitrogen (and phosphorus) entering waterways from irrigation return drains and in surface run-off from agricultural land is believed to be very different, with the nitrogen from irrigation drainage being generally much more available.

KEY POINTS

- The major sources of nitrogen are from sewage treatment plants, stormwater, agricultural activities, forests and the atmosphere.
- Inputs from point sources, such as STPs, are the easiest to manage, although the reduction targets to be achieved can vary depending upon the receiving ecosystem.
- Stormwater sources can contribute high nutrient loads, although management of these sources can be difficult because of their highly pulsed nature. Several best management guidelines for managing stormwater are now available.
- Diffuse agricultural sources of nutrients are very difficult to manage. Methods are available for estimating the relative nutrient loads from the different sources in agricultural catchments. However, these are generally too crude to provide specific advice and further do not provide information on the bioavailability of the nutrients.
- Timber plantations and farm forestry activities are expanding rapidly in many Australian States. Nutrient inputs from these sources are poorly known.
- Nitrogen inputs from groundwater, the atmosphere and natural forests (particularly mature mountain ash forests) are the most difficult to manage.

Question 3: Are the available management strategies for each of these major sources effective? Do we know enough now to assist managers?

The workshop concluded that there is a great deal of information available on best-practice management strategies for urban sources of nitrogen (eg. STPs, urban stormwater), and that this information is now increasingly available. However, nitrogen generation from non-point sources, particularly agriculture and commercial forestry activities, is less well quantified and, while information on best management practice is available, it is generally poorly organised.

The workshop concluded that there is currently sufficient information to make a start on the development of best management practice guidelines for both point and diffuse sources of nitrogen, and that adaptive management practices should be adopted for different catchments and ecosystems within these catchments. A first and urgent need is the preparation of best-management practice manuals specifically related to the management of nitrogen sources. Adoption of best-management practice guidelines is also critically important, especially (for diffuse sources) when dealing with large numbers of individual landholders. The workshop recognises that N management requires proper consideration of socio-economic as well as scientific/ technical aspects. The workshop recommends examination of the potential for split-applications of N fertilisers, timed to match peak periods of crop or pasture demand. This activity is practised to some extent but should be reviewed to determine the feasibility for wider adoption.

In managing non-point sources of nitrogen, the workshop noted two important differences between nitrogen and phosphorus. First, the only effective way to remove nitrogen is through biological processes (cf. P removal which can be either physical (sedimentation), chemical (adsorption) or biological). Recent overseas work (Alexander et al., 2000) suggests that removal of nitrogen via denitrification is much more efficient in smaller rather than larger streams. Second, the fate of nitrogen is largely controlled by hydrological processes and transport pathways (cf. P fate controlled largely by particle transport), and there could be scope for controlling nitrogen removal by increasing the transport pathways

The workshop recommended that programs aimed at managing nitrogen should carefully define the desired ecological outcomes and then use these to develop possible nitrogen reduction targets. It was noted that more work is needed to define the ecological effects caused by excessive concentrations and loads of nitrogen in particular aquatic systems.

KEY POINTS

- There is now sufficient information on best management practices (BMP) for urban sources (STP, stormwater), and these BMP guidelines are generally readily available.
- Nitrogen generation from diffuse agricultural sources is not well quantified, although in a number of situations these can be a large source.
- There is clearly a large amount of knowledge on how best to manage these diffuse nutrient sources, but this needs to be better organised to make it more available for managers.
- In managing N and P, two important differences should be considered: biological methods are the only effective way to remove N, and the fate of N and P are controlled by different processes (P controlled by particle transport, N controlled by hydrological processes and transport pathways).

Question 4: How well linked are N and P? Can P management strategies adequately address N as well or do we need to do more? If more can we specify? What are the links between N management and management of other environmental factors?

The available evidence is that nitrogen and phosphorus processes are not particularly well linked, although a number of the generally adopted phosphorus management techniques can also affect nitrogen removal.

Nitrogen exists in more forms than phosphorus, and these forms are generally more mobile in the environment. The main dissolved forms of nitrogen include organic-N, nitrate and ammonium. Ammonium and nitrate are the forms most readily used by phytoplankton and benthic micro-algae, although organic-N can be converted to ammonium and nitrate by bacterial processes, and thereby be made available.

In a number of systems, the usefulness of managing total-N concentrations has been questioned. For example, although the levels of bioavailable nitrogen (ammonium, nitrate) may be a small proportion of the total-N, if the rates of nitrogen mineralisation and uptake are high, reduction in the concentrations and loads of total-N may have little effect on the ecological effects.

Best management guidelines for phosphorus management are now available, and a number of these techniques should also work in reducing the loads of nitrogen. These include: buffer strips[1] and destratification of standing waterbodies (lakes, reservoirs and weir pools).

Nitrogen reduction from STPs will be needed, although as indicated above, it will be most important to ensure that the nitrogen concentrations are not reduced to such a level that nitrogen-fixing cyanobacteria are preferentially selected over other, preferable, algal species. Land disposal of sewage effluents is the preferred option in much of inland Australia. However, the potential for the more soluble forms of nitrogen (eg. nitrate) to be transported to the groundwater and then into wetland and streams must be considered.

Wetlands are important systems for removal of nitrogen, mostly by denitrification of nitrate. Managers should consider the re-establishment (or restoration) of wetlands and floodplain systems as a means for reducing nitrogen loads to waterways. There is some evidence suggesting that wetlands are more efficient at removing nitrogen (and phosphorus) if it is possible to restore the natural wet and dry cycles.

In Western Australia, the use of slow-release phosphate fertilisers has been adopted by the farming community with impressive results (Humphries & Robinson, 1995). The workshop has noted that the slow-release nitrogenous fertilisers currently on the market are far more expensive than alternatives and hence unlikely to gain widespread usage, especially in broad-acre farming. Consequently, the workshop recommends investigation into low-cost, slow-release N fertilisers.

The Workshop recommended three general principles related to nitrogen management:

- Biological processes (eg. denitrification, biological uptake) are the most effective in removing N, and these can be enhanced in wetlands, buffer strips and small tributary streams.
- Where possible, management strategies aimed at removing nitrogen should be linked to other management strategies (eg. salinity control, phosphorus control, water quality).
- For most systems, the loads of BOTH nitrogen and phosphorus entering waterways will need to be controlled. In freshwater systems, both nitrogen and phosphorus may control algal growth, but in almost all cases, the algal biomass (or yield) is controlled by the amount of available phosphorus.

1. These are most effective when used along the small tributary streams. There is still a need for research to show the most effective buffer strips for removing nitrogen.

KEY POINTS

- The available evidence suggests that catchment N and P processes are not particularly well linked, although a number of the generally adopted P management techniques can also result in some N removal.
- Three general principles related to N management were identified:
  - Biological processes (eg. denitrification, biological uptake) are the most effective in removing N, and these can be enhanced in wetlands, buffer strips and small tributary streams;
  - Management strategies aimed at removing N should be linked to other management strategies (eg. salinity, phosphorus, water quality);
  - The loads of BOTH N and P entering waterways need to be controlled in most systems.

Question 5: What nitrogen reduction targets should we be aiming for?

The available evidence shows a trend towards significant increases in nitrogen use by Australian agriculturalists. Unfortunately, there is currently a lack of knowledge to assist resource managers in deciding what (if any) nitrogen reduction targets are needed. Such decisions are of course closely linked to the ecological outcomes or environmental values that the community wishes to maintain in the system being managed.

Managers generally require two types of information in order to set targets for the levels of nitrogen reduction needed to achieve particular ecological outcomes (eg. a low frequency of cyanobacterial blooms):

- Knowledge of the transport and transformation processes affecting nitrogen within a catchment. Although there is considerable general understanding about these processes, there are no models available that can predict the amount of nitrogen that will be processed within a particular catchment. R&D is needed to obtain this knowledge.
- Biological effects caused by the catchment-derived nitrogen once it enters a waterbody. The ability to predict the ecological effects of nitrogen within a particular waterbody is probably a little better than for catchment predictions, but even this is still in its infancy.

The Workshop was equivocal about the usefulness of TN:TP ratios as a management tool. Unfortunately, in many Australian freshwater systems the TN:TP ratio does not accurately reflect the biologically available nitrogen and phosphorus concentrations. Thus use of the TN:TP ratio is a rather blunt management tool at best.

The Workshop recommended that a more productive direction would be to develop guidelines and decision support tools that included the following information:

- the bioavailable nitrogen and phosphorus concentrations—methods are now available for measuring the bioavailable fractions (Robards et al., 1993; McKelvie, 2000).
- Whether the system is presently P-limited or N-limited—methods are now available to rapidly assess the nutrient limitation status of a waterbody (Wood & Oliver, 1995).
- The relative concentrations of the various nitrogen species (eg. ratios of $[NH_4^+]/[NO_3^-]$ and $[NH_4^+ + NO_3^-]$/[Dissolved organic-N]—as noted above there is now evidence suggesting that these ratios may influence the algal species composition.
- Conceptual models of the interactions between nitrogen (and phosphorus) and the various physical, chemical and biological factors that can influence the algal species composition in a particular freshwater system. Simple risk-based decision support tools are available for phosphorus (ANZECC/ARMCANZ, 2000), but these need to be extended to also include nitrogen. A number of other useful decision tree relating these factors are available (Oliver & Ganf, 2000; Oliver et al., 2000). Work is also under way to extend these decision trees into predictive models.

The Workshop suggests that the focus should be on managing nitrogen (and phosphorus) concentrations to minimise local effects at low flow, with the focus on managing loads to minimise downstream effects (eg. in standing waterbodies and estuaries).

KEY POINTS

- The current trend is towards significantly increased N use in Australian agriculture.
- Targets for the levels of N reduction should be based on specific ecological outcomes desired (eg. a low frequency of cyanobacterial blooms).
- This will require information on the *likelihood of sufficient N being generated and transported within the catchment, and the ecological consequences caused by the catchment-derived N once it enters a waterbody*
- The focus should be on managing N (and P) *concentrations* to minimise local effects at low flow, with the focus on managing *loads* to minimise downstream effects (eg. in standing waterbodies & estuaries).
- Several decision support tools are available (eg. AEAM, ecological risk assessment) that could be used to assist managers make decisions on the required N reduction targets.

Question 6: What are the opportunities for management intervention in the nitrogen cycle?

The Workshop identified a number of management principles that could assist resource managers in minimising the adverse effects of nitrogen in freshwater ecosystems. These include:

- Approach nitrogen management from a systems (catchment) perspective.
- Attempt to identify all major sources of nitrogen, quantify the loads contributed from each source, when the inputs occur (all through the year or after rainfall), and whether the nitrogen is present in bioavailable forms.
- Prioritise the sources in terms of the adverse ecological effects they cause, and aim to manage the high priority sources first.
- Leave natural systems essentially unmanaged (this mainly refers to forested areas).
- Always attempt to focus the main management practices as close to the source of the nitrogen as possible (source control).
- Make every attempt to manage nitrogen within the catchment as it is much more difficult to manage once it enters the waterways.
- Identify and manage (and perhaps restore) the most important parts of the system where denitrification (the main process for removing nitrogen) is likely to occur (wetlands, small tributary streams).
- Be sensible about the time scales required to effect changes as a result of particular management actions—these can be very long (decades) depending upon the sediment stores of nutrients.

KEY POINTS

- A number of management principles were identified that could assist resource managers in minimising the adverse effects of N in freshwater ecosystems.
- Nitrogen management should be approached from a systems or catchment perspective.
- In order to set nutrient management priorities for a catchment, it is necessary to identify the major N (and P) sources, quantify the loads transported (& what time of the year this is contributed) and how much of the load is in bioavailable forms.
- It is good management practice to manage nutrients as close to the source as possible, and as far as is possible within the catchment (management becomes more difficult once nutrients enter a waterway).
- There may be scope to reduce losses from N fertilisers by developing cost-effective, slow-release N fertilisers; slow-release P fertilisers have been adopted by the farming community in Western Australia with impressive results.
- It is good management practice to protect (and perhaps restore) wetlands, small tributaries and riparian vegetation, as these are likely to be the parts of the catchment where most N reduction occurs.
- The time to rehabilitate degraded systems may be quite large (eg. decades), and this needs to be factored into nutrient management plans.

5 Research and development needs

THE WORKSHOP participants identified the following high priority R&D needs:

- Commission a R&D project to develop a conceptual model of typical catchments and attempt to quantify the sources, loads and budgets; nitrogen fixation should also be considered in the N budget.
- Commission a R&D project to develop hierarchical decision tools to predict the ecological consequences of excessive N levels in priority ecosystem types.
- Commission a knowledge exchange project to ensure that the new methods for measuring N limitation are more available to resource management agencies.
- Commission a critical review of the relative loads and bioavailability of N from a range of different agricultural sources.
- Commission a critical review of the relative importance of natural forests, forestry activities and commercial tree plantations in contributing N (and P) to catchments.
- Commission a critical review of the effectiveness of the available catchment loading models for estimating N budgets for different catchment types.
- Commission a knowledge exchange project to draw together currently available knowledge for diffuse nutrient sources and to use this to develop best management guidelines. In particular, methods for potentially increasing N removal by increasing hydrologic pathways (eg. passing run-off through wetlands, buffer strips and intact tributary streams) should be reviewed.
- Commission a R&D project to investigate the potential control of algal species composition through manipulation of the N speciation (eg. dissolved inorganic N/dissolved organic N ratio).
- Commission a R&D project to investigate important aspects of denitrification in Australia freshwater systems, this to include: the role of benthic micro-algae (also snags, biofilms and macrophytes) in enhancing N removal, the role of small tributary streams in N removal, and the effectiveness of natural and artificial wetlands in removing N.
- Commission a R&D project to assess and further develop a suite of decision-support tools to assist catchment managers to identify appropriate ecological objectives for priority ecosystems, and to set nutrient reduction targets to achieve these objectives.
- Commission a R&D project to determine how best to restore wetlands and floodplain systems such that N removal processes (wet/dry cycles, denitrification, uptake) are re-established.
- Commission n R&D project to determine the best methods for measuring the bioavailable forms of N.
- Commission a R&D project to determine the role of intact tributary streams in removing N (by denitrification), and the changes in this process if these tributaries are degraded.
- Commission a review to assess the potential for effective and slow-release N fertilisers to be produced.

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Part II: Appendixes

Appendix A. Nitrogen workshop program

Day 1

0900–0920 Introduction, objectives, outputs (Hart, Davis)

0920–1050 *Management perspectives*
Series of presentations (7 × 10 min) reviewing current knowledge about possible ways in which management might intervene to reduce the adverse effects of nitrogen. What are the key management questions regarding nitrogen in the freshwater environment?
Pat Feehan
Peter Vollebergh/Graham Rooney
Gary Bickford
Anna Bailey
Heather Hunter
Christine Coughanowr
Tom Rose
Summary (Koop – 20 min)

1050–1130 Morning tea

1130–1230 *Sources*
Series of presentations (3 × 15 min) reviewing current knowledge about the relative importance of the major sources of nitrogen and the potential for management interventions to reduce these inputs.
Mick Meyer
Heather Hunter
Peter Breen
Discussion and summary (Davis – 15 min)

1230–1330 LUNCH

1330–1515 *Transformations*
Series of presentations (6 × 15 min) reviewing current knowledge about the key transformation processes involved in nitrogen dynamics in inland water ecosystems (eg. nitrification, denitrification, nitrogen fixation)
James Udy
Phil Ford
Paul Boon
Darren Baldwin
David Hamilton
Ian Webster
Discussion and summary (Hart – 15 min)

1515–1535 Afternoon tea

1535–1710 *Effects*
Series of presentations (5x15 min) reviewing current knowledge about the uptake of nitrogen by phytoplankton, attached algae, benthic algae (microphytobenthos) & macrophytes in inland waters.
Bill Dennison
Rod Oliver
Brett Light
Jane Roberts
Justin Brooks
Discussion & summary (Grace – 15 min)

1710–1740 *General discussion & summary – Hart*
Summarise the key points to emerge during the day, and outline the program for Day 2.

1930– DINNER

Day 2

0900–0945 *Group discussion*
Each of the above groups get together to discussion whether the summary and key points brought out truly reflect the current knowledge base in that area.

0945–1000 Morning tea

1000–1300 *Working groups*
Break into four small groups (each made up of researchers and managers). Each group to address two questions:
What are the opportunities for management intervention in the N cycle?
As a consequence of such management interventions, what are the key R&D gaps that need to be filled?

1300–1400 LUNCH

1400–1540 *General session (facilitator– Hart)*
Report back by each group (4 × 10 min)
General discussion on management interventions and R&D needs.
Put these into priority order.

1540–1600 Summary (Hart)

1600 Workshop close (Hart) & Afternoon Tea

Appendix B

Workshop participants

Name	Affiliation
Anna Bailey	Dept. of Land & Water Conservation, Barwon Region, NSW
Dr Darren Baldwin	Murray–Darling Freshwater Research Centre, Albury
Gary Bickford	Sydney Water Corporation
Dr Paul Boon	Victoria University of Technology, Melbourne
Dr Peter Breen	Melbourne Water & CRC Freshwater Ecology
Dr Justin Brookes	CRC for Water Quality & Treatment, Salisbury, SA
Dr Sophie Bourgues	Water Studies, Monash University & CRC Freshwater Ecology
Peter Cottingham	CRC Freshwater Ecology
Dr Christine Coughan	Dept. of Primary Industries, Water & Environment, Tasmania
Dr Richard Davis*	CSIRO Land and Water
Dr Bill Dennison	University of Queensland
Pat Feehan	Goulburn–Murray Water, Tatura, Victoria
Dr Phillip Ford	CSIRO Land and Water
Dr Mike Grace*	Water Studies, Monash University & CRC Freshwater Ecology
Dr David Hamilton	Centre for Water Research, University of WA
Prof. Barry Hart*	Water Studies, Monash University & CRC Freshwater Ecology
Dr Heather Hunter	Dept. of Natural Resources, Queensland
Dr Klaus Koop*	NSW EPA
Dr Brett Light	Marine Sciences, Victorian EPA
Dr Carl (Mick) Meyer	CSIRO Division of Atmospheric Research
Dr Mark O'Donoghue	Water Studies, Monash University
Dr Rod Oliver	Murray–Darling Freshwater Research Centre, Albury
Dr Jane Roberts	CSIRO Land & Water
Dr Graham Rooney	Melbourne Water
Tom Rose	Water & Rivers Commission, WA
Dr James Udy	Centre for Catchment and In Stream Research, Griffith University, Qld
Peter Volleburgh	Dept. of Natural Resources & Environment, Victoria
Dr Ian Webster	CSIRO Land and Water

*Organising committee member

Appendix C

Contributed papers

Managing nitrogen — a manager's perspective

Pat Feehan

Manager Natural Resources, Goulburn–Murray Water, Tatura

Introduction

In this paper I attempt to provide an overview of:

- the strategic direction for nutrient management in the Goulburn–Broken catchment;
- why we chose to concentrate on P rather than N management;
- background information about nutrients in the catchment; and
- finally, pose some questions that, if answered, could provide management direction.

The Goulburn–Broken catchment and water quality strategy

The Goulburn Broken catchment covers 2.3 million ha or about 10% of Victoria. The upper parts of the catchment produce a water resource of 2,800,000 ML which is used for a variety of purposes in the Murray Valley, Shepparton, Central Goulburn and Rochester irrigation areas, and by other users further to the west and downstream along the Murray River. The network of food-processing industries in the Goulburn Valley leads to its recognition as one of the nation's food bowls. Roughly 50% of the catchment is used for dryland agriculture (cropping and grazing), about 30% is forested and the balance is irrigated.

The Goulburn–Broken catchment is one of three high priority catchments targeted by the Murray–Darling Basin Ministerial Council's Algal Management Strategy to develop and implement catchment management strategies addressing algal and nutrient problems. The Goulburn–Broken Water Quality Working Group (WQWG) and the Catchment Board's River and Water Committee coordinated development of the water quality management strategy for the Goulburn–Broken Catchment. The strategy was finalised in April 1997.

The objectives of the strategy are to:

- minimise blue–green algal outbreaks within the Goulburn–Broken catchment thereby reducing risks to public health, industry and water users;
- minimise nutrient contributions to the River Murray (and reduce the risk that our nutrients will cause or contribute to algal blooms downstream);
- enhance the riverine environment;
- foster regional development; and
  minimise/optimise water treatment costs.

To achieve these objectives, the strategy initially concentrates on:

- phosphorus reduction activities, especially those which can quickly achieve cost-effective reduction of nutrient loads reaching the River Murray;
- P reduction over the summer, low-flow period to reduce the risk of algal blooms within the Goulburn–Broken catchment; and
- P load reduction. Within most of the Goulburn–Broken catchment, nutrient concentrations in waterways are not a major issue, but the nutrient loads carried by the streamflows are very important.

Why focus on phosphorus?

- The decision to concentrate on P management was based on the view promoted by Harris (1996): "All the evidence points to the fact that by far the best course is to reduce external P loadings (and increase the TN:TP ratio by that means) rather than attempt to change N loadings...").
- The difficulty of achieving a strategy that focused on reduction of two nutrients rather than one.
- A view that it would be a lot harder and more expensive to achieve effective N reduction (although it was recognised opportunities to reduce other nutrients, such as N, would also be pursued, when they are cost-effective, can be associated with phosphorus management and can be shown to reduce the risk of blue–green algal blooms.

Nutrient sources

As part of developing the strategy, estimates of nutrient sources within the catchment were made (Table 1), based on AEAM and CMSS models and information derived from background investigations.

Note that irrigation drains are a major source of P, while dryland diffuse is the overwhelming source of N. Within the dryland (diffuse), atmospheric N, associated with rainfall, was identified as a major source.

Nutrient generation, or export, rates

Dryland

Table 2 gives a summary of nutrient generation rates for several dryland catchments.

Wet/dry year ratios

Parts of the catchment were subject to severe flooding in 1993. Nutrient loads in 1993 were compared with loads in 1994 (a drier year) (Table 4). The very high ratio of almost 10 for TN loads in some catchments indicates that

Table 1. Key nutrient sources (estimated, typical year)

Nutrient source	Phosphorus (TP) (t)		Nitrogen (TN) (t)	
Irrigation drains	169	47%	619	21%
Dryland (diffuse)	110	30%	1866	65%
Sewage treatment plants	50.5	14%	184	6%
Intensive animal industries	30	5%	141	5%
Urban stormwater	12.3	3%	70	2%
Total	371.8		2,880	

Table 2. Summary of revised dryland catchment nutrient generation rates

Sub-catchment	Length of data record (years) used to calculate loads	Catchment area (ha)	Average generated loads ($kg\ ha^{-1}\ yr^{-1}$)		Average nutrient load (t/y^{-1})	
			TP	TN	TP	TN
Broken R at Moorngag	8	49,700	0.09	1.45	4.5	72
Hollands Ck	8	45,100	0.10	1.48	4.6	66
Murrindindi R	8	10,800	0.09	2.23	1.0	24
Acheron R	8	61,875	0.11	2.10	6.9	130
Sunday Ck	5	33,700	0.04	0.76	1.2	25
Delatite R	8	36,800	0.12	1.97	8.7	72
Goulburn R (upstream Jamieson)	5	69,400	0.05	0.56	3.6	39
King Parrot Ck	8	18,100	0.04	1.14	0.7	21
Seven Ck at Pollie McQuinns	6	15,300	0.12	3.46	1.9	53
Seven Ck at Euroa	5	33,200	0.16	2.81	5.4	93
Sugarloaf Ck	5	60,900	0.03	1.29	1.6	78
Castle Ck	5	16,400	0.11	1.53	1.8	25
Brankeet Ck	5	12,100	0.06	0.93	0.7	11
Big R	8	33,300	0.07	1.34	2.5	44
TOTAL		496,675			45.1	753

Notes:
- The range of TN generation rates from a high of 3.46 kg/ha/year for Seven Ck to a low of 0.56 for the Goulburn river upstream of Jamieson.
- Some catchments with a high proportion of forest (eg. Acheron, Murrindindi and Delatite) (Table 3) have high TN generation rates.
- There is not always a happy coincidence of high TP generation rates with high TN generation rates. Such a coincidence would simplify development of catchment strategies.

TN loads in wet years are very high and that management options would have to cope with large variation. Wet year management options could well be very expensive.

Dryland nutrient concentration compliance

Nutrient concentration

Available nutrient concentration data from the dryland parts of the catchment has been assessed against various guideline figures.

Australian Water Quality Guidelines for Fresh and Marine Waters (ANZECC guidelines). For rivers and streams, indicative concentrations values of ranges are:

TP 0.01–0.1 mg/L

TN 0.1–0.75 mg/L

Available concentration data have been assessed against the upper limits of the ANZECC guidelines for rivers and streams. The percentage of records greater than the guideline figure for TN and TP is shown in Table 5.

Only the Goulburn River at Eildon, the Acheron River at Taggerty, Sunday Creek at Tallarook and the Big River always meet the TN guideline limit.

EPA Guidelines. The EPA has prepared preliminary nutrient guidelines for Victorian streams (Tiller and

Table 3. Catchment land use (estimated visually)

Sub-catchment	Dominant land uses	Estimated land use (%)	
		Forest	Grazing and broad-acre cropping
Seven Ck at Euroa	Pasture	10	90
Seven Ck at Pollie McQuinns	Pasture	10	90
Murrindindi R	Forest	100	0
Delatite R	Pasture, forest	50	50
Hollands Ck	Pasture	70	30
Acheron R	Pasture, forest	85	15
Broken R at Moorngag	Pasture, forest	20	80
Big R	Forest	100	0
King Parrot Ck	Pasture, forest	85	15
Brankeet Ck	Pasture, forest	50	50
Goulburn R (upstream Jamieson)	Forest	100	0
Sunday Ck	Pasture	60	40
Castle Ck	Pasture/ cropping	0	100
Sugarloaf Ck	Pasture	10	90
TOTAL			

Note: pasture includes grazing/broad acre cropping.

Table 4. Nutrient generation rates and wet/dry year ratios

Catchment	TP 93	TP 94	Wet/dry TP	TN 93	TN 94	Wet/dry TN
Broken R at Moorngag	0.22	0.03	7.3	3.26	0.35	9.3
Hollands Ck	0.17	0.02	8.5	2.31	0.22	10.5
Murrindindi R	0.13	0.07	1.9	2.95	1.84	1.6
Acheron R	0.15	0.08	1.9	2.85	1.53	1.9
Delatite R	0.09	0.04	2.2	1.34	0.35	3.8
King Parrot Ck	0.05	0.02	2.5	1.7	0.62	2.7
Seven Ck at Pollie McQuinns	0.13	0.06	2.2	3.74	1.89	2.0
Seven Ck at Euroa	0.22	0.04	5.5	4.41	0.85	5.2
Big R	0.09	0.04	2.2	1.8	0.88	2.0

Newell 1995). This gives recommended nitrogen and phosphorus concentrations for seven river regions across the State with similar environmental attributes and stream systems. Within each river region, available biological and nutrient data were collated, allowing an assessment of background, threshold and 'major impact' nutrient concentrations.

Water quality data have been assessed against the EPA guideline criteria in the VWQMN Annual Report 1997 (Water Ecoscience 1998). For the Goulburn–Broken catchment, an average attainment of 25% was obtained for TN (30 sites) versus 52% for TP (29 sites).

One presumes from this that the state of water quality with respect to N must be pretty bad!

Trends

Nutrient concentration data were recently analysed for trends (Smith and Nathan 1999). Data from nine stations were analysed. There were insufficient data to discern regional trends. Trends detected for TN were small, negative and were detected at three of the nine sites analysed. Two of these trends were significant at the 5% level, while the other site was significant at the 10% level.

Catchment generation rates—irrigation

In irrigation drainage water, nutrient concentration are generally high (median concentrations TP in the range 0.3–0.6 mg/L; TN 1.1–2.4 mg/L). Export rates for TP were around 0.8 kg/ha and for TN 3.0 kg/ha. Harrison (1994) found substantial differences in TP:TN ratios for pasture and horticulture.

Summary

In summary:

- P sources are different to N sources;
- the atmosphere is a large source of N;
- large bursts of N are associated with high flow—therefore difficult to treat; and
- large loads of N come from forested catchments—minimal treatment options are available

Management issues

- *Relative importance of N versus P*
  How important is N in controlling BGA blooms and should we now be concentrating on N management as well as P management?
  What is the relative importance of managing N versus P for other reasons (eg. aquatic environment)?

- *What are the diffuse sources of N?*
  Where is all the N coming from, especially in dryland areas—is it possible to do anything about it?
- *N targets*—how much do we need to achieve?
- *Management options*—what cost-effective N management options exist, especially for diffuse sources?
- *How good are the guideline figures?*

Table 5. Percentages of records in which ANZECC guidelines for total nitrogen and total phosphorus are exceeded

Site	Percentage of records with TN greater than 0.75 mg/L	Percentage of records with TP greater than 0.1 mg/L
Seven Cks at Polly McQuinns	100	0
Castle Ck at Arcadia	100	100
Seven Cks at Euroa	95	0
Broken Ck at Rices Weir	94	100
Broken Ck at Katamatite	92	88
Broken River at Moorngag	78	0
Goulburn River at McCoys Bridge	77	55
Broken River at Goorambat	64	34
Goulburn River at Shepparton	55	11
Brankeet Ck	37	0
Hollands Ck at Kelfeera	30	5
Goulburn River at Murchison	29	1
Broken River at Gowangardie	27	9
Goulburn River at Seymour	22	4
Delatite River	12	4

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Overview of nitrogen management issues in Victoria

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Introduction

In this paper, I present a brief overview of some aspects of 'nitrogen (N) management' from my perspective as a manager and policy-maker. Note this is not a complete picture, as there are many activities with which I am not familiar.

The paper will briefly deal with:

- overall State-wide policy and planning frameworks that include nitrogen management (State Environment Protection Policy (SEPP), Victorian Nutrient Management Strategy, water quality monitoring);
- N trends and compliance with guidelines;
- current N-related investigations and research being undertaken within the Department of Natural Resources and Environment (NRE); and
- conclusions about the status N management in Victoria.

State Environment Protection Policy

The *State Environment Protection Policy (Waters of Victoria)* (SEPP (WoV)) was declared in 1988. It establishes broad water quality objectives for the management of Victoria's surface waters. It does this by specifying the beneficial uses to be protected and by defining the objectives for a number of water quality indicators to protect these uses.

In regard to nutrients, the policy states "Waters shall be free of substances in concentration which cause nuisance plant growth or change in species composition to the detriment of the protected beneficial uses". Clearly, it is difficult to define what levels of phosphorus (P) or N meet this objective.

There are also about 12 SEPPs or schedules to SEPP (WoV) which consider individual waterbodies, catchments or regions within Victoria. Less than half of these SEPPs specify N objectives, covering only three catchment management authority (CMA) regions (Corangamite, Wimmera and West Gippsland). Compliance against the objectives will be assessed in Section 4.

Victorian Nutrient Management Program: framework for catchment-based nutrient plans and other management actions

The State Government released the *Nutrient Management Strategy for Victorian Inland Waters* in March 1995. Its objective is to: "provide a policy and planning framework to assist local communities and the state government manage nutrient levels in waterbodies in order to minimise the potential for the development of algal blooms, particularly blue–green algae". The strategy was developed in response to the large algal blooms that occurred in south-eastern Australia in the early 1990s.

It recognises that P and N are major nutrients that limit algal growth. But the strategy also adds, "with phosphorus being considered the most important nutrient contributing to algal growth". Note that, as a policy framework, and not a definitive technical document, it was careful to say "*considered* the most important".

The major focus of the strategy was the development of catchment-based nutrient management plans/strategies in 'problem' catchments around Victoria. There are currently 18 plans in some stage of development or implementation, covering nearly all of Victoria. Oversight of development and implementation is by the catchment management authorities. The Goulburn–Broken strategy is covered in more detail in another presentation.

Many of the plans have not formally discriminated between N and P management in their objectives, but implicit in their priority setting processes is a focus on P. For example, the methodology used to assess the economic costs and benefits of nutrient plans focuses on P reductions to waterways. Those that do explicitly focus on P, such as the Goulburn–Broken, still acknowledge the importance of managing N. They often make the point that N and P management is related ie. minimise P input to waterways with management practices and you are often minimising N input also.

Plans that explicitly focus on P include: Upper North East, Ovens, Goulburn–Broken, Campaspe, Loddon, Wimmera and Central Gippsland.

Examples of typical principles from these plans:

- "The Strategy will initially focus on P reduction (although where possible, N will be addressed concurrently)"; and
- "The main priority of the Strategy is the reduction of total phosphorus concentrations and loads…"

The reasons for focusing on P are dealt with in more detail by the Goulburn–Broken presentation and partly relate to the reason for this workshop, namely the understanding to date about the role of P as opposed to N in algal bloom formation in freshwater systems.

It must also be remembered that the emphasis of most nutrient management activity has been on minimising the potential for algal bloom development, particularly (often toxic) blue–green algae. Given that many (but not all) blue–green algae can fix their own N, it was (still is?) important to manage P entering waterbodies. The message acted upon by managers, put crudely and simply, was: even if many freshwater systems are N limited, they are effectively P limited for N-fixing toxic blue–green algae, so you'd better manage P.

There are some exceptions among the nutrient plans. The Corangamite nutrient plan does not discriminate between N and P. With many shallow lakes with 'groundwater driven' hydrology in the region, the plan is particularly interested in the impacts and management of N (see reference to Woady Yaloak research below).

The Yarra and Werribee rivers flow into Port Phillip Bay. There is a statutory (SEPP) objective to reduce N inflow to the Bay by 1000 t/year by 2006. Thus, the priority management actions of the Yarra and Werribee plans have N as an important focus. Consistent with the theme already discussed, Werribee focuses on P management within the catchment, to lower the risk of blooms in water supply storages in the catchment, while it focuses on N contributions to the Bay.

The East Gippsland nutrient plan will also consider N, given that it is concerned with inputs to the Gippsland Lakes, an estuarine environment.

I have also been informed that preliminary results from the Portland Coast (SW Victoria) nutrient plan indicate that the waterways of the catchment may be N limited, not P limited (but I have not seen any data or analyses).

The nutrient plans summarise the contributions to total nitrogen (TN) and total phosphorus (TP) load by different land-uses (see Goulburn–Broken presentation). In catchments without irrigation areas, the proportions contributed by any land use to TP and TN load are broadly similar. This is not the case in irrigation areas (as noted in Goulburn-Broken example), where proportionately more N comes from dryland pasture, and more P from irrigation drains.

Compliance with SEPP and guidelines

Compliance against SEPP, ANZECC and/or EPA nutrient guidelines has been examined in most of the plans (eg. Goulburn–Broken presentation).

Compliance against SEPP objectives is low in Corangamite, and medium–high in the West Gippsland and Wimmera catchments.

In 1995, as part of the State's Nutrient Management Strategy, the Environment Protection Authority released nutrient guidelines (TN and TP concentration maxima at base flow) which characterised six regions of Victoria with sufficiently similar rivers and streams. The TN maxima range from 0.15 mg/L in 'pristine' mountain regions to 1.0 mg/L in urban areas and south-western Victoria. These are basically within the range of the 'old' ANZECC values for TN in rivers and streams (0.1–0.75 mg/L).

Compliance for TN against these EPA nutrient guidelines is quite variable across the State but, consistent with the Goulburn–Broken example, many of the lowland streams have poor compliance with the EPA or ANZECC guidelines, often below 50%. Upland streams usually have greater than 90% compliance. On a CMA basis, compliance against EPA N objectives was often low (in 1998, in 7 of 10 CMA regions average compliance with N objective was <50%; Wimmera and Glenelg Hopkins are the only two regions with higher [but still reasonably poor] compliance; no data for Mallee). Compliance for TP is generally better.

Trends

The Victorian Water Quality Monitoring Network includes more than 150 surface water sites at which TP and TN concentrations are measured monthly. Over 90 of these have more than 10 years of data, so could be used for trend analysis. While TP trends at these sites are virtually zero on average across the State, TN shows average trends between –0.04 and 0.04 mg/L/year. Note, however, that some *individual* sites across the State show significant and quite large upward TP trends.

There are significant (to 5%) small–medium downward trends in TN (ie. up to 0.025 mg/L/year) at many sites across the State, particularly in the Port Phillip, North East and East Gippsland catchments. On the other hand, sites in the Corangamite/Barwon and Westernport/South West Gippsland regions show significant (to 5%, some to 10%) upward trends in TN (up to 0.05 mg/L/year; one site in Corangamite has an upward trend of 0.147 mg/L/year TN).

In regard to groundwater, N (as nitrate) levels over 30 mg/L (ANZECC upper limit for drinking water quality is 10 mg/L) occur in the western suburbs of Melbourne, at Point Nepean (Mornington Peninsula), in the Warrnambool–Tower Hill area, around Lake Corangamite and in the Ovens Valley. What impact do these high groundwater levels have on N levels in the waterways of these catchments (and Port Phillip Bay)? Certainly, preliminary work in the western district indicates that groundwater may be a very important source of N to the region's waterways, particularly the shallow lakes (and particularly in summer when blooms are more likely to occur).

Note that there is currently no coordinated program of groundwater quality sampling.

In summary, considering the compliance and trend data, it would appear that TN concentrations in streams are 'poorer than' TP levels. What does this mean, for general river health and for possible algal bloom development?

Research

There is a range of catchment-based, groundwater and agricultural related research currently being undertaken in Victoria in relation to N. This section reviews some of the research. It is *not* comprehensive, and to some extent, the work covered and the extent to which it is covered, relates to how much I could find out about it!

- *The impact of baseflow quality on stream water quality in the Woady Yaloak catchment* (NRE, Sinclair Knight Merz)

  The study concluded that "if baseflow and groundwater nutrient concentrations in the Woady Yaloak catchment are any indication, surface waters in the Corangamite, Barwon and Moorabool basins may be affected by groundwater discharge". However, it also concluded "The TN load to surface water from baseflow is generally not considered to be significant on an annual basis. However the daily load of TN to streams from baseflow would be more significant during periods of low stream discharge".

  Primary contact: Heather Adams, NRE Colac, 03 5233 5548.

- *Best management practices for N in intensive pasture production systems* (NRE, University of Melbourne, Dairy Research and Development Corporation, other sponsors).

In summary, there is a need to increase pasture production for an expanding dairy industry in south-eastern Australia. Application of higher rates of N fertiliser may be an option. However, the environmental impacts of unsustained N fertiliser use in intensive grazing systems in south-eastern Australia is poorly known, hence this project aims to:

1. formulate practical management guidelines to minimise nitrogen losses while maintaining productivity in dairy pastures in south-eastern Australia;
2. evaluate a range of existing simulation models for their applicability to N cycling in grazed dairy pasture systems in south-eastern Australia; and
3. identify critical gaps in information essential for refining the foregoing two aims.

As well as the guidelines and simulation model, the project should result in knowledge of the rates of N loss from temperate, high rainfall and flood irrigated dairy systems.

The project includes a number of component projects. One specifically looking at nitrate leaching is indicating that nitrate N concentrations are low below the root zone during water movement and that N leaching is low, *in dry years.* There is a need to continue to run the project in wet years and look at lighter soil types.

Primary contact: Richard Eckard, Ag Vic Ellinbank, (03) 5624 2219. See website: <www.nitrogen.landfood.unimelb.edu.au>.

How is the research transferring to management actions? Through decision-support systems to be used by farm advisers/consultants/extension staff. Management messages will be delivered through the Target 10 dairy extension program.

Nitrogen use in the strawberry runner and strawberry fruit industries (NRE, Melbourne Water). N usage by some annual horticultural crops in the Port Phillip region is proving to be very high, compared with perennial and grazing industries. Melbourne Water monitoring has previously picked up N as an issue in two sub-catchments dominated by annual horticultural industries.

Movement of N below the root zone in the strawberry runner and strawberry fruit industries needs to be better assessed. A project is proposed to commence next financial year.

Investigation of groundwater as a nutrient source to shallow lakes in the Corangamite region (with particular reference to Lake Murdeduke) (NRE and The University of Melbourne). Investigation to determine the impact of groundwater on water quality of shallow lakes. A final report is due in May 2000.

Primary contact: Heather Adams, NRE Colac, 03 5233 5548.

- *Environmental impact of high input pasture systems* (NRE). This project aims to determine N and P losses from high, medium and low input grazing systems. Measurements of losses in north-eastern Victoria have been completed. Preliminary findings indicate that while P losses are low from all the trial catchments, N losses show greater range and can be quite high (1.0–10.4 kg/ha). Most of this is as deep drainage, but there is also significant surface and subsurface flow.

  Nutrient management guidelines for high rainfall zones to cover dryland grazing industries and to develop principles for cropping systems will be produced during 1999–2000.

  Primary contact: Anna Ridley, NRE Rutherglen, 02 6030 4500.

Note that there are many other research and investigation activities being undertaken within NRE aimed at considering nutrient impacts of various agricultural activities which often consider both N and P movement, concentrations, loads etc. These should lead to the development of better management practices and guidelines for these activities. The Victorian Nutrient Management Program Annual Report attempts to summarise these projects.

Conclusions

This section will briefly provide answers to the questions posed by the workshop from my perspective as a manager/policy-maker regarding nutrient issues.

Does N pose a threat?

Not according to many of the individual plans, which focus on P. But in some regions, where N trends are upward (c/f P stable) and there is definitely non-compliance with N guidelines, a threat by N is suggested. Also, groundwater N appears to be a threat to surface waters in some regions, particularly in western Victoria. We probably don't know in many cases, although we know it is a threat in Port Phillip Bay.

We also rely on scientists to inform us about the relative importance of N in algal bloom formation. Thus, as noted earlier, the concept of N-limited freshwater systems may not matter for N-fixing blue–green algae.

What management actions are currently being directed towards this issue?

On-ground nutrient management priorities are being determined through nutrient management plans (as outlined above), which focus primarily on P. Perhaps not many are specifically aimed at N, except in a few catchments, but there is the understanding that many of the priority P management actions will also reduce N. There is considerable management effort at developing nutrient related best management practice guidelines for a range of agricultural and urban activities.

With particular relevance to N, management effort has been directed at:

- N fertiliser application and pasture management, particularly in high-input pasture systems and in areas with sandy soils;
- managing dairy shed waste in regard to protecting groundwater; and
- managing nutrient and water inputs to the sandy soils of the Mallee (as there is no surface run-off and N is the major nutrient reaching the Murray through sub-surface drainage).

What N-related research programs are being undertaken in your area?

Research is covered above. How well does the 'agricultural' research link with the 'environmental' research?

What are the key information gaps that would help management of N?

Is N a 'problem'? If it is, how much of a problem (ie. do we know what N targets we need to achieve to prevent algal blooms (same problem for P))? Are the P management actions definitely managing N also? What cost-effective management actions are suitable for N? How significant is groundwater contribution of N to surface concentrations/ loads, particularly in certain parts of the State?

Is the information you need getting through to you from the scientists?

Difficult to answer. In some cases, yes, eg. the applied research programs noted above where extension is part of the project design. In other cases, probably not. It is difficult even to determine what research is going on. It also appears that there is a lack of connection between the 'agricultural research faction' and the 'environmental research faction' that leads to mixed management messages getting through from the scientific community.

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Many draft, catchment-based nutrient management plans.

Overview of nitrogen management issues in the greater Melbourne region

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Introduction

Waterways and the catchment of the Port Phillip region are a major source of contaminant loads to Port Phillip Bay. Nutrients, metals, organic compounds, litter and pathogens enter the bay through over 350 waterways and drains. While toxicant-related issues have occasionally surfaced in Port Phillip, most management concerns have centred on litter and bacteria at beaches, and eutrophication effects from exceeding a particular nutrient-load ceiling.

The eutrophication concern was the driver behind the Port Phillip Bay Environmental Study, conducted by CSIRO over the period 1992 to 1996 (Harris et al., 1996). For some years, nitrogen (N) was suspected as the crucial nutrient for managing the health of Port Phillip, and this suspicion was confirmed with the completion of the study. It predicts that there is a critical nutrient load at which phytoplankton growth rates will lead to eutrophication of the bay—an event that may have irreversible impacts. While there is considerable uncertainty about the nature of this critical load, the study recommends that priority be given to load reductions of N.

The recently revised Port Phillip Bay State Environment Protection Policy (SEPP) requires a nutrient reduction plan as a component of an overall environmental management plan for the bay. The SEPP establishes a target for reduction in annual N loads to Port Phillip of 1,000 tonnes. This is consistent with recommendations from CSIRO, although its emphasis was on catchment contributions and a reduction in storm overflows.

We acknowledge that N loads and concentrations do represent an issue for waterways, but our strategy is to concentrate on Port Phillip. It is assumed that any gains made in reducing loads to the bay will have local and regional waterway benefits.

Agency strategies and plans

For over two decades, government has actively pursued the reduction of nutrient loads in the Port Phillip region. The 1997 Port Phillip and Westernport Regional Catchment Strategy establishes, as a key outcome, the reduction of nutrient loads to the bay, with a performance indicator being "compliance with SEPP environmental quality objectives". Several *Catchment Action Plans* have recently been released by the Catchment and Land Protection Board that identify actions which provide a basis for the long-term management of waste that affects water quality, particularly that contributing to excess levels of nutrients.

Operational planning and implementation consistent with these plans and strategies is the responsibility of a number of organisations. While the bay nutrient reduction plan will outline broad load targets and reporting and review arrangements, it will not recommend specific actions to achieve load targets.

There is currently no agreed program for achieving the nutrient reduction in relation to catchment loads, or any indication of the feasibility of different options. There is also no clear indication of the costs and benefits of nutrient reduction programs and thus no clear process for the allocation of funds. A tool is needed to assist with the selection of options, including at least some rudimentary cost–benefit analysis.

Catchment loads and land use

Catchment loads are highly variable in time. For instance, in most Australian river systems 80–90% of the contaminant loads discharge in less than 10% of the time (Harris, 1994). This would also apply to the Yarra River, where episodic events are related to outbreaks of localised algal blooms, particularly in Hobsons Bay. CSIRO calculated that flows from catchment waterways carry a total annual load to the bay of around 2,750 t of N (Harris et al., 1996). This is equivalent to 37% of the total load of N discharged to the bay each year.

Researchers and natural resource managers realise the potentially large annual variability in water quality. Pettigrove (1997) calculated that a total load of 2249 t of

N was discharged from the Yarra River during 1993 and 1994: 1594 t (71%) during 1993 and the remaining 655 t (29%) during 1994. The differences reflect the variation in the annual volume of flow in the two years. A majority of N (59%) came from the middle and upper, mostly rural, sections of the Yarra catchment and 40% from urban segments. Urban-area load contributions appear to increase significantly during wet periods. The non-estuarine Maribyrnong River reach contributed around 177 t N/yr during 1993 and 1994. Almost this entire load is generated from rural land use.

Based on 1993–94 estimates, sewage treatment plants (STPs) contributed a little over 100 t/yr, or from 7% to 16% of the total load in the Yarra River catchment. STPs in the Werribee River catchment use land disposal and are assumed to contribute no load. The Altona STP currently discharges around 62 t N/yr. Sewage spills from emergency relief structures built into the sewerage network have been estimated for the Yarra River catchment in 1993–94, and make up less than 2% of total loads.

Groundwater contributions to stream inputs in the Port Phillip catchment have been estimated to be a high as 20% as a base-flow component and 50% of the total flow of the Yarra River. A historical estimate of groundwater contribution is 55 t N/yr—rated as “negligible” by CSIRO (Harris et al., 1996).

Load trends

Generally speaking, water quality in waterways and the bay has improved significantly over the last 20–30 years, chiefly as a result of catchment-sewering programs and improvements in sewage treatment. With the exception of a small number of STPs, point-source discharges have been largely eliminated. Further efforts to improve catchment water quality will therefore need to focus more on diffuse sources of pollution, such as urban stormwater and rural run-off.

While existing loads of nutrients from forested catchments can be expected to remain much the same over the next 20 years, growth in population, expansion of urban areas and changes in rural land use have the potential to increase catchment nitrogen loads.

The contribution of urban areas to N loads in the Werribee catchment is expected to increase from the current 25% of total to 63% of total by the year 2025 (an increase in N load entering waterways in the Werribee basin from 71 t/yr to approximately 116 t/yr)(Cottingham et al., 1997, page v).

Estimates of the increase in N load associated with population increases and urban growth in Melbourne are shown in Table 1. Clearly urban growth will create considerable pressures on nutrient loads to the bay.

There are no data on the changing pattern of rural land use and its likely impact on catchment water quality. Any increase in land-use intensity, such as the conversion of grazing land to viticulture with greater cultivation and use of fertilisers and water, is likely to increase loads from these areas.

Issues for managing nitrogen

The FILTER model

Analysis of existing water quality data provides some indications of the geographic origins of many water quality problems. In the Port Phillip catchment, the effectiveness of source controls or structural treatment measures in reducing pollution loads is not well understood. In addition, the extent to which individual actions integrate to provide catchment-wide changes is difficult to predict.

Accordingly, FILTER was developed to support decision-making on programs for the improvement of stream water quality in waterways in the Port Phillip catchment and the reduction of pollutant loads to the bay. FILTER is a simple, GIS-based, sediment and nutrient load, concentration and areal generation rate computer program for the Port Phillip catchment. The FILTER model has the capacity to allow managers to examine the effects of various interventions and remedial actions on

Table 1. Nitrogen load changes with increasing urbanisation

Year	Urban area (km^2)	Urban percentage of catchment	Urban run-off (GL/yr)	N load[b] (t N/yr)
1930	350	4	200	680
1960	800	8	420	1,428
1990	1500	23	950	3,230
2020[a]	2100	32	1,200	4,000

a Figures for 2020 are estimates, derived from Melbourne Water growth forecasts
b Based on a mean N concentration in urban run-off of 3.4 mg/L (Duncan 1999, Table 3)

local and whole-of-catchment loads and concentrations of nutrients and sediments.

FILTER can contribute to the identification of sources and structural control options to achieve water quality objectives, allow estimates of program costs and predict likely changes in water quality (concentrations and loads) arising from such programs. Developing FILTER has been a joint project. Participants are Melbourne Water (Waterways and Drainage), the Port Phillip Catchment and Land Protection Board, the Environment Protection Authority and the Department of Natural Resources and Environment (DNRE).

The next stage is to analyse the economic costs and benefits of nutrient-load reduction in the Port Phillip catchment. A project involving Melbourne Water and DNRE representatives is currently under way to tackle this stage. The FILTER project will identify potential measures to reduce nutrient loads through improvements in rural land management, sewerage system operations, incorporation of stormwater treatments in new urban development, and retro-fit of stormwater treatments in existing urban areas. After estimating load reductions likely to result from these actions, a key step will be comparing loads with potential catchment loads for the year 2020, were there no management intervention. Key outputs from the project are the costs of damages associated with nutrient loads in the Port Phillip catchment and a discussion of the management actions that are likely to represent the best investment in reducing the economic risks associated with these loads.

Urban run-off

The increased volumes and velocities of run-off in urban areas causes a significant increase in the amounts of material (loads of pollutants) carried by the flow. Combustion products and activities such as transportation and construction, provide abundant sources of pollutants that are readily available for wash-off from the relatively impervious urban surfaces. Run-off carries these pollutants into drains, waterways and the bay.

Within existing urban areas there are limited opportunities to mitigate these effects. The major proportion of pollutant loads is delivered during high-flow events. Effective treatment often means capturing large volumes of stormwater moving at high velocity. Treatment to remove nutrients requires long detention times for sedimentation, filtration and nutrient uptake. This requires large land areas for temporary storage of run-off—generally up to 2% of the catchment area. Suitable areas of such land are rare in most urbanised catchments, although suburbs developed since the 1960s often have significant floodplain reservations which have some potential for incorporating stormwater treatment.

In developing urban areas—so called 'green-fields'—the opportunities are greater, except where the topography is unsuitable. Redevelopment in existing urban areas, which results in increased building densities and impervious areas, is likely to increase catchment loads with little if any opportunity for mitigation

The most cost-effective strategies for load reduction in existing urban areas are likely to be source controls involving improved operational practices by local government, business and households, with some opportunity for stormwater treatments in post 1960s areas with significant areas of reserved floodplain.

In green-field situations, water sensitive urban design and stormwater treatment measures can be employed to minimise load increases. Both structural treatment measures and source controls for improving stormwater quality have been outlined in the recent *Best Practice Environmental Management Guidelines for Urban Stormwater*. The performance objectives in the guidelines should become a requirement for all new development in the Port Phillip region.

Given the limitations on stormwater treatment within existing urban areas and the expected expansion of urban areas over the next 20 years, it is unlikely that significant overall load reductions will be achieved. This point is highlighted in Table 2, which compares the contributions of the various sources of N and their expected trends—if existing management programs remain.

Accordingly, system planning and design will be an important tool to help support adoption of water-sensitive approaches to stormwater management in new developments. A decision-support system (DSS) for urban stormwater is being developed by the Cooperative Research Centre for Catchment Hydrology. A useful DSS can be used by all end-users, including the developers.

Atmospheric contributions

Nitrogen loads from atmospheric sources in the catchment of the bay have not been determined with any accuracy, but are likely to be considerable. From the bay study, CSIRO (Harris et al., 1996) estimated that the annual contribution was over 1,000 t N/yr (14%) directly to the bay. In the Chesapeake Bay in the eastern United States, atmospheric deposition accounts for 27% of the catchment non-point-source load. We really don't know how much new material reaches our watercourses by dry deposition, but we do know it exists, and we do know that it is mostly of relatively local origin. At a practical level, the understanding and management of emissions to air is obviously going to be important.

Air-shed modelling during the development of the Port Phillip Air Quality Management Plan will estimate whether an increase in emissions will occur in the future.

Sewerage system up-grade

Most population increases in the Port Phillip catchment will be connected to the sewer, with treatment provided by the Western Treatment Plant discharging direct to Port Phillip or the Eastern Treatment Plant discharging to Bass Strait. Flows from local STPs in the Yarra River catchment are increasing at about 1% per year. Any increases in discharge from STPs will be offset by expected improvements in treatment performance to reduce loads. The Western Treatment Plant is predicted to reduce N loads discharging to Port Phillip Bay by 500 t over the next seven years.

There is evidence that the sewerage system is contaminating some waterways, but no estimates of possible loads from this source are available. Human faecal contamination is relatively common in drains. The source of this contamination could be illegal connections of household sewers to stormwater drains, sewer overflows or leaking sewers. Large sections of the considerable pipe network that makes up the sewerage system are aged and possibly deteriorating. New monitoring technologies being evaluated by Melbourne Water may help to assess potential loads from this source.

In unsewered areas, septic tanks are the main form of sewage treatment. The performance of these systems is very dependent upon site conditions and proper maintenance. Currently no data are available to determine the contribution of discharges from on-site treatment systems on the total nutrient load from the Port Phillip catchment. Backlog sewering programs are expected to reduce contamination from this source in the future.

A small reduction in loads to the bay could be achieved by reducing the N load discharged from STPs. In 1993–94, STPs in the Yarra River catchment, for example, contributed about 100–110 t N/yr. Decommissioning of some plants and improvements in treatment reduced this load to around 78 t by 1997–98. Other STP closures by 2004 may mean that N loads from STPs in the Yarra catchment may be reduced to about 50 t N/yr in 2006.

Rural land management

Rural land in the Port Phillip catchment exports a greater proportion of the total catchment nutrient load to the bay than urban land, simply because of its larger land area. Land-management practices, such as stocking rates, cultivation and fertiliser application, affect nutrient and sediment generation. The design and maintenance of rural roads can also affect nutrient and sediment generation. Improved land management can reduce loads.

Implementation of on-farm measures related to pasture improvement, filter strips, revegetation and fertiliser application in the Werribee catchment is estimated to provide N load reductions of around 10 t N/yr. The YarraCare Working Group (1996) estimated that the

Table 2. Sources of nitrogen in the Port Phillip catchment

Source	Current estimated contribution to load[a]	Expected trend based on programs currently in place	Comment	Reductions in N loads from improved catchment management
Groundwater	<5%	Increase slightly	No short-term intervention possible	–
Atmosphere	>20%	Increase slightly	Increasing emission standards should compensate for growth—assumed that vehicle emission standards will maintain existing loads	?
Treatment plants	~10%	Decrease significantly	Improvements to treatment plant performance or diversion to Bass Strait will compensate for growth	–150 t N/yr
Rural land use	45%	No change	Some intensification of land use eg. viticulture assumed	–80 t N/yr
Urban land use	35%	Increase significantly	Based on growth forecasts loads may increase by another 300 t or 10% by 2006	0 to +15 t N/yr
Forested land use	10%	No change		–

[a] Figures do not total 100% because there is some overlap of sources; eg. atmospheric emissions contribute to catchment loads of N which are measured in run-off quality.

widespread adoption of best-practice land management could reduce nitrogen loads by as much as 15% or 60 t/yr.

Conclusions

Management needs to address the three main sources of loads to waterways and the bay:

- STPs and sewage contamination;
- urban run-off; and
- rural land management.

Further reductions in contaminant loads from the catchment will be achieved only by upgrading stormwater systems and reducing diffuse sources of pollution while ensuring that new urban growth and development does not further increase loads.

Several opportunities exist to reduce loads of N and other pollutants in the Port Phillip catchment within the next decade. These include:

- encouragement of best practice in urban and rural land management (eg. farm management and operational activities of local government);
- adoption of best practice planning and design of stormwater systems;
- treating run-off through the use of wetlands and other devices where shown to be cost effective;
- improving vegetation in the riparian zone and other strategic areas to filter run-off; and
- preserving natural waterways to enhance the denitrification process.

Given the trend of increasing N loads resulting from urban development and population growth, sustaining a significant long-term reduction in loads will be difficult to achieve. Storm events of the kind assumed to trigger occasional blooms in Hobsons Bay are particularly difficult to control given the large volumes of run-off to be treated. Significant reductions in N loads and other contaminants, however, could be achieved through a determined program of source control and stormwater treatment in the catchment. Given the likely contribution of air emissions to catchment N loads, the potential for load reductions from this source should also be further examined.

Options for cost-effective achievement of reductions in catchment contaminant loads are currently being assessed as part of a catchment water quality modelling project (FILTER). The proposed EPA air-shed modelling to be undertaken as part of development of the Port Phillip Air Quality Management Plan, should be used to identify the possible benefits of emission controls.

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Managing nutrients in the Hawkesbury–Nepean River

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Abstract

The management of nutrients in the Hawkesbury–Nepean River has been addressed by considering point and non-point contributions to waterways, population growth, other demands on sewage effluent quality such as disinfection and toxicants, and the social benefits and economic costs of these improvements.

Sydney Water has undertaken a detailed assessment of the long-term wastewater management options for the Hawkesbury–Nepean catchment. These options address improving water quality, protecting public health, servicing substantial population growth and providing cost-effective solutions. The process links water quality objectives to strategic decision making in wastewater management.

Introduction

Sydney Water Corporation provides wastewater services to approximately 500,000 people in the Hawkesbury–Nepean catchment. The population is served by 17 sewage treatment plants (STPs) that discharge a total average dry weather flow of 142 ML/day of effluent into the Hawkesbury–Nepean River and tributaries. Discharges range from 0.1 ML/day at the smallest STP to 38 ML/day. STPs not operated by Sydney Water contribute about 5 ML/day to the Hawkesbury–Nepean River.

Water quality is a significant issue in the catchment. The river is subject to prolonged periods of low flow (80% of the time) punctuated by periodic high flows. The low-flow periods, together with high nutrient concentrations, make the river vulnerable to eutrophication particularly during summer.

Water quality in the river has significantly improved over the past 10 years. Upgraded treatment at STPs has resulted in significant reductions of phosphorus and nitrogen (particularly ammonia). However, water quality is compromised with respect to nutrients, faecal contamination, pesticides and other pollutants from point and non-point sources that affect ecosystem and public health.

In addition to STP sources, nutrient inputs via leaking septic tank and other sewerage systems are a significant problem in the Hawkesbury–Nepean catchment. Some of the major contributors are leaking or overloaded septic systems (eg. those servicing caravan and ski parks located near river banks) and the siphoning and overflow of on-site systems into stormwater drains and local watercourses.

The New South Wales Department of Urban Affairs and Planning has predicted the population in the Hawkesbury–Nepean catchment will increase to more than one million by 2021. It is estimated that this population will require treatment up to 300 ML/day of sewage effluent.

The wastewater planning process

Ecologically sustainable development (ESD) was adopted as a key principle in the planning process for developing options for improved sewage management. The planning time frame used to develop the options is 20 years. The process comprises several key steps:

- identify environmental values;
- specify water quality criteria to meet these values;
- determine current and future nutrient loadings to meet water quality criteria;
- identify management options to meet these criteria;
- assess social and economic issues;
- rank options; and
- implement management actions.

Extensive community consultation was used to derive environmental values. The most important issues were ecosystem protection and primary contact recreation. The water quality criteria to meet these values for ecosystem protection (primarily with respect to algal growth) and public health protection were based upon ANZECC (1992) guidelines. Specific phosphorus (P) and nitrogen (N) levels at each STP were determined to meet chlorophyll-*a* criteria. Dynamic water quality models were used to establish the relationship between water quality criteria and the nutrient loads required to meet these criteria. In association with these investigations for nutrients, studies were undertaken to assess impacts from pathogens and potential toxicants in effluent. Ecological and human health risk assessments were carried out following USEPA protocols (Sydney Water, 1996). Follow-up studies utilising toxicity assessment and toxicity identification and evaluation methodologies were used to identify specific chemicals causing toxicity.

The study examined whether changes to STP performance alone could meet the water quality criteria.

The options developed were:

- advanced wastewater treatment for nutrient removal with discharges within the catchment;
- maximised effluent treatment and recycling (potable and non-potable) within the catchment;
- decentralised treatment and effluent recycling of all dry weather flows in new development areas (in response to some community preference for decentralised treatment); and
- effluent transfer out of the catchment for use over the Blue Mountains in inland areas or for disposal to the ocean.

Social and environmental benefits were assessed using a multi-criteria analysis approach in conjunction with economic considerations based on the principles of ESD.

Results of planning studies

All options were able to achieve the required water quality criteria for the predicted population growth in 2021 and are summarised in Table 1.

The reduction of algal blooms, now and in the future, is key to the delivery of the long-term wastewater strategy. Phosphorus reduction strategies have been identified as the most effective in reducing algal blooms and nuisance macrophyte growth—N reduction will also be achieved. Phosphorus loads at the STPs need to be reduced so that concentrations in effluent are less than 0.15 mg/L in most situations. Some STPs require reductions as low as 0.03 mg/L. These options can be achieved through existing technologies, although they will be pushed to the limit. At two STPs discharging into Berowra Creek, significant reduction of both N and P is required as the discharge occurs close to an estuarine reach of the Hawkesbury River where the role of N is regarded as more significant.

Modelling of wet weather performance of STPs in the Hawkesbury–Nepean catchment indicates effluent bypassing the sewage treatment process contributes to degraded water quality. Overflows from the sewerage system are not a significant cause of water degradation in wet weather.

Management actions

The larger STPs are being upgraded to reduce levels of nutrients, and some of the smaller STPs will be closed and flows transferred for more cost-effective treatment at a larger STP.

Total P load discharged to the Hawkesbury–Nepean River by Sydney Water's STPs in 1998–99 was approximately 55 kg/day compared with 240 kg/day in 1989–90 (Fig. 1). Further improvements in STP treatment will reduce P levels to 35 kg/day in 1999–2000. Nitrogen loads have reduced from 3100 kg/day in 1989–90 to 1700 kg/day in 1998–99. Further N reductions will occur at many STPs over the next 3–4 years, reducing effluent concentrations to 10 mg/L or less. Nutrient levels in effluent discharging to Berowra Creek will be reduced to 0.1 mg/L total P and 3 mg/L total N.

Table 1. Options for achieving required water quality criteria in the Hawkesbury–Nepean River

Option	Cost ($m)	Comment
Advanced treatment and discharge	420	Technology currently available and proven—provides for recycling in the future Social/environmental benefits equal to or greater that other options Financial risk is low
Treat and recycle	620	Technology currently available but not proven in all cases Overall environmental and social benefits are mixed Ability to conserve water is offset by high cost of materials, land and energy
Decentralised option	1400	Decentralised treatment alone will not achieve nutrient load targets Social/environmental outcomes are less favourable than most other options
Effluent transfer	450–2000	Technology is simple and reliable Treatment cost low but transport costs very high Social/environmental benefits equal to other options Financial risk is high

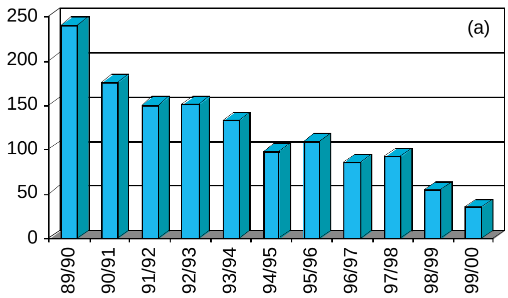
A significant amount of research and development is addressing the need to consistently deliver these low levels of treatment. These activities include the use of online analysers and novel control of STP processes.

Much effort has been made to identify desired levels of P and N in STP effluent to reduce algal blooms. More needs to be understood about diffuse source inputs. An adaptive management approach will be necessary to determine cost effective and sustainable solutions to nutrient management in the river system. Monitoring of the river will be maintained to determine if the management actions identified in this strategy will deliver the required water quality outcomes. Outcomes of this monitoring will be used to reassess the level of nutrient reduction required and should provide information on non-point source impacts and ecosystem recovery times.

An example of nutrient improvements at three STPs is shown in Table 2 to indicate the changes over the past decade. Costs are increasing to deliver the higher levels of nutrient reduction required to protect the river. For example, the 3 mg/L nitrogen reduction target at West Hornsby and Hornsby Heights STPs will require a capital investment of $26m. These two STPs serve 100,000 people.

Future research needs

The upgrading of STPs alone has substantially decreased some nutrient species. However, there is a need for more work to relate the water quality data to the contribution of intrinsic assimilative processes. The lack of uniformity of trends, such as those between the South, Cattai and Berowra creek tributaries, underlines that systems can behave differently. Therefore, management of the



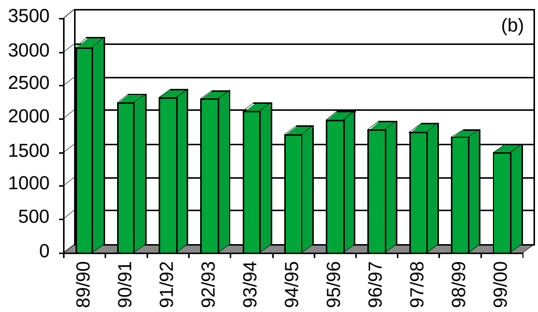


Figure 1. Total phosphorus (a) and nitrogen (b) loads discharged into the Hawkesbury–Nepean River by sewage treatment plants, 1989–1990 to 1999–2000

Table 2. Nutrient reductions in sewage effluent achieved at three sewage treatment plants in the Hawkesbury–Nepean catchment

STP	Upgrade	Date	Effect on effluent quality
West Camden	Pickle liquor dosing	1983–86	Total phosphorus reduced from 6 mg/L to 1 mg/L
	Multi point dosing	1994	Total phosphorus reduced from 1 mg/L to 0.2 mg/L
	Alkalinity addition	1993–95	Ammonia reduced from 15 mg/L to 1 mg/L
	Anoxic zones for denitrification	1990–91	Total nitrogen reduced from 40 mg/L to 18 mg/L
	Optimisation, dissolved oxygen control	1997–98	
	Tertiary clarifier	2003	Total nitrogen reduced from 18 mg/L to 13 mg/L
	Anoxic capacity plus	2003	Total phosphorus reduced from 0.1 mg/L to 0.04 mg/L
	Aerobic digesters		Total nitrogen reduced from 13 mg/L to 7.5 mg/L
Penrith	Amplification of BNR reactor	1989	Total phosphorus reduced from 6 mg/L to 2 mg/L
			Ammonia reduced from 30 mg/L to 5 mg/L
			Total nitrogen reduced from 30 mg/L to 6 mg/L
		1994–95	Total phosphorus reduced from 2 mg/L to 1 mg/L
	Alum post dosing	1999–2000	Total phosphorus reduced from 1 mg/L to 0.1 mg/L
	Deep bed sand filters	2003–04	Total phosphorus reduced from 0.1 mg/L to 0.09 mg/L
	Stage 8 Amplification		
West Hornsby	Pickle liquor dosing	1983–86	Total phosphorus reduced from 6 mg/L to 1 mg/L
	Multipoint dosing	1993	Total phosphorus reduced from 1 mg/L to 0.1 mg/L
	Alkalinity addition	1993–95	Ammonia reduced from 15 mg/L to 1 mg/L
	Anoxic zones for denitrification	1993	Reduced total nitrogen concentrations from 40 mg/L to 25 mg/L
	Increased anoxic zones with methanol addition	2002	Total nitrogen reduced from 25 mg/L to 3 mg/L

Hawkesbury–Nepean system will still need to be carried out on a site-specific basis.

In the case of point sources for nutrients in the Hawkesbury–Nepean River system, there is considerable documentation on the loads derived from STPs and some stormwater systems. Conversely, much less is known about loadings derived from different land-use areas and the relative impact that this has compared with point sources. Attempts have been made to model these types of diffuse inputs. There is still considerable effort required to make the models accurate to quantify points or non-point sources to determine the priority areas for nutrient reduction.

The measurement of nutrient concentrations and loads over time does not give a good understanding of ecosystem function. While insights can be gained from such measurements, these are limited to snap-shot perspectives and provide little information on the dynamics driving an ecosystem or the biogeochemical processes maintaining it. Despite this, the majority of investigations conducted on the Hawkesbury–Nepean River involve little to no process measurements. This trend is currently changing but the available information is still deficient in this characteristic.

There has been little measurement of water column or benthic nutrient remineralisation or dynamic processes. Again, some work has been undertaken in this area, but in view of the type of management questions being posed concerning sustainable loads and nutrient impacts on ecosystem components, there is a clear need to significantly enhance our understanding in this broad area of nutrient dynamics process.

The level of sophistication now possible with models allows for the upward and downward scaling of models that was once far more difficult. This could be used in dialogue with management to both refine the questions being posed and the modelling approach taken to deal with the particular issues.

Conclusion

Planning undertaken by Sydney Water has identified a range of management actions to reduce algal blooms, provide more effective disinfection and reduce toxicants in sewage effluent. The preferred options were identified through a process that balanced environmental, economic and social benefits. An adaptive management approach will be used to assess the success of these improvements and the need for future P and/or N reductions

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Managing nitrogen in the Namoi catchment

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Introduction

Work on nutrient management in the Namoi catchment to date has largely concentrated on the management of phosphorus; its sources and movement through the system. Little specific attention has been given to nitrogen (N). However, water quality programs in the catchment have recognised its importance as a river contaminant and N data have been collected in routine sampling programs. Through these data we can draw together some information about the level of N in our waterways and some knowledge about its sources.

Briefly outlined below are the possible threats posed by N to the waterways of the Namoi, current water management actions directed towards N issues, N-related research being undertaken in the Namoi, key information gaps and comments on communication of scientific research results. As an introduction to the issue in the Namoi catchment, a brief overview of current knowledge on the levels of N in our streams and some of its possible sources is included.

The Namoi catchment and nitrogen

The latest results from a major water quality program in the Namoi catchment *(Central and North West Regions Water Quality Program (CNWRWQP), 1998–99)* showed that there was no downstream trend of increasing N. It did, however, highlight significant increases downstream of Tamworth and Narrabri sewage treatment plants (STPs). A study of water quality on the Liverpool Plains did detect an increasing trend downstream in Mooki and Coxs creeks and concluded that this was mainly linked to higher use of fertilisers in the lower catchment of these creeks.

Levels of N detected by the CNWRWQP in 1998–99 sampling year at some points throughout the catchment did exceed the 1992 ANZECC guidelines for prevention of excessive algal growth and so triggered more detailed studies of the aquatic ecosystem. The levels of N were in the order of 2500 μg/L in the Namoi River at Mollee, and 1100 μg/L in the Peel River at Bective. These sites do display consistently high levels.

The 1998–99 CNWRWQP also found a significant positive relationship between N and flow at many sites in the Namoi, with flows from Coxs Creek and the Mooki River in the Liverpool Plains carrying significant levels of fertiliser and sediment, particularly during storm events. Levels of total N in the lower catchment at Weeta Weir and Bugilbone also rose sharply during the major flooding in winter and spring of 1998–99.

The Liverpool Plains Water Quality Project showed, through its storm sampling, that there were significant amounts of N detected in the first flush of a storm event. Storm events play a large role in the transport of sediment and nutrients into the rivers and streams of the Namoi catchment. A flood event in 1996 in the Mooki catchment transported some 90 t of N past one sampling station, along with an estimated 350,000 t of soil.

The CNWRWQP 1998–99 reported possible increasing trends in total N from mid-1991 to mid-1999 for the Peel and Namoi rivers at various locations.

Sources of nitrogen in the Namoi catchment

Analysis of water quality data from the Namoi could lead us to believe that the STPs at Narrabri and Tamworth are significant sources of N in the Namoi catchment. Other point sources—such as intensive animal industries and saleyards—would also be contributing.

The diffuse sources of N are obviously large contributors to the rivers and streams in the Namoi. The Liverpool Plains Water Quality Project showed that the presence of N in surface water on the Liverpool Plains was likely to be related to the use of fertiliser on both summer and winter crops. High rates of anhydrous ammonia, urea, and sulfate of ammonia are used in the catchment. Nitrogen application rates are generally in the range of 60–30 kg per hectare, depending on crop and soil type.

The smaller levels of N coming from the upper catchment areas in the Liverpool Plains, as compared to the lower catchment, would be a result of the smaller area treated with N-based fertilisers as compared to the floodplain cropping areas. Other diffuse organic sources of N commonly include animal manure, pasture and crop residues, and these may also be contributing to N levels in the catchment.

Threat of nitrogen now or in the future

The continued degradation of water quality in the Namoi poses various future threats, such as excessive algal blooms and disruption to aquatic ecosystems. Water quality objectives for the Namoi catchment identify that good quality water is needed for ecosystems, swimming, watering stock, irrigation and domestic use. The valley relies on its water for financial security of its communities and values a sustainable, biodiverse river. Increasing levels of N may pose a threat to any of these uses and values of the river systems in the Namoi in the future.

Current nitrogen management practices in the Namoi catchment

There are few if any management practices in the Namoi solely directed towards N management. However, current soil conservation management practices that restrict and reduce soil erosion and movement in the valley are all contributing to reducing the movement of N into waterways. The use of tail-water return systems on irrigated cropping areas also reduces the amount of N entering the river, as do other best management practices such as buffer strips, filter strips, riparian zone management and fertiliser application according to best management practice.

There has been a priority upgrade of sewage treatment plants in the Namoi, which has led to Gunnedah now having land disposal of its effluent and Narrabri and Tamworth soon to go off-line.

Several other programs that are operating in the catchment may contribute to the management of N. These include:

- stormwater management plans;
- adoption of conservation farming practices;
- nutrient management planning;
- best management guidelines for cotton farmers; and
- planning activities by the River Management Committee to address water quality objectives.

Many of these on-ground management activities and planning actions consider N management as a component of their objectives.

Research programs relating to nitrogen

There are no specific N-related research programs known to be operating in the Namoi catchment. There are, however, several water quality monitoring programs that have collected or are collecting N data: the Central North and West Regions Water Quality Program (CNWRWQP); the Integrated Monitoring of Environmental Flows (IMEF) project; the first National River Health Assessment; the Storage Water Quality Program; the Key Sites Water Quality Monitoring Program; and localised studies such as the Liverpool Plains Water Quality Project completed in 1998.

There are some management-based research programs that include investigations into nutrient management, but these are just beginning or, in some instances, at the stage at which funding has been applied for. A Grains Research and Development Corporation program in the Liverpool Plains area will look in particular at farm scale sources and at mechanisms for transport at the catchment scale, and will endeavour to evaluate management options to reduce nutrient transport and provide management guidelines.

Information needed to improve management of nitrogen

Some of the key information gaps that management in the Namoi Valley may be faced with in the future will revolve around the development of a plan to address water quality objectives in the catchment.

The following are some of the areas of concern that could be addressed to help management:

- How serious are the future threats related to increasing N levels: what’s the worse case scenario; what’s the most likely?
- What threats does N pose to groundwater systems in the future?
- Confirmation of transport pathways of N in aquatic environments and the relative contribution of nitrogen based fertilisers.
- Do management practices related to soil conservation, fertiliser management and land effluent disposal adequately address the issues on increasing N levels in our aquatic ecosystems, including groundwater?
- Does N retain its source identity through the system?
- How do different sources of N break down in the aquatic environment and are there varying levels of effect depending on the resulting residue? That is, what indicators should be used in monitoring programs for nitrogen?
- What role will increasing N levels in the Namoi Valley play in our algal management strategies?

- Does the management of N help in the control of algal blooms in the Namoi catchment? Is N important, and to what level compared to other elements, in the control of algal blooms in the Namoi catchment?
- Will land application of effluent from STPs create increased problems in the future for management of nutrients, including nitrogen?

Information and communication pathways

Information pathways between science and management will always be a concern that must be addressed. Long-term research results are valuable and are needed to increase our understanding of the systems that we live in and influence. We must be aware that communities and resource managers are charged with the task of developing plans and carrying out actions that will maintain or improve the quality of our water. Scientific support of these present requirements must be maintained. Current information on technical actions required to address the issue of N in the Namoi catchment and many other catchments throughout New South Wales and Australia must be developed for immediate use. Ongoing communication and update of these actions and information surrounding the issue must be continued over time.

Managers specifically require clear and concise management directions from research. Common concerns are those of mixed messages depending on the scientific information accessed. It is workshops such as the one reported on in this volume that will help to put out a common message to managers. Managers continually ask for plain-English management outcomes from research. These would be most useful in the form of summaries of current knowledge and background information to enable managers to make informed decisions.

The issue of changing water quality trends will always be an on-ground one to encourage uptake of better management practices. It is through the uptake of the outcomes of current and future R&D that changes will occur. There is sufficient information out there now to know that soil erosion management practices and fertiliser application best management practices will most likely help to reduce the amount of N entering our river systems. These changes are not occurring to the rate that would be anticipated and required to maintain our current water quality status. Financial support of research into how to get uptake of R&D outcomes by land managers is possibly now more than ever money well spent in terms of improving catchment management. The time frames for change are becoming increasingly short as our resources degrade.

Nutrients in the Derwent estuary catchment

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Nutrients in the Derwent River

The Derwent River is one of the largest rivers on south-eastern Tasmania, with an average yearly flow of approximately 120 cumecs and a catchment area of nearly 9000 km^2. The Derwent River is used for municipal and industrial water supplies in Hobart, hydropower generation and irrigation. In addition, it is the main source of fresh water to the Derwent estuary.

Nutrients have been the primary focus of a three-year study of the Derwent and its catchment, which commenced in 1996 with funding from the National Landcare Program. The goals of this study include monitoring nutrient concentrations in the river and its tributaries under a range of flows, determining total nutrient fluxes from the river to the Derwent estuary and identifying major nutrient sources.

During the first year, monthly 'baseflow' water quality monitoring was carried out at four sites along the main stem of the Derwent and near the downstream end of its nine major tributaries. At each site, in situ measurements were made of temperature, conductivity, dissolved oxygen, pH and turbidity. Water samples were collected and analysed for total suspended solids (TSS), nitrogen (NO_x-N, NH_3-N, TN) and phosphorus (PO_4-P and TP). During the second year, sources of elevated nutrients were investigated in two tributaries—the Tyenna River and the Clyde River.

On the whole, the Derwent River was shown to have relatively low levels of nutrients, turbidity and TSS, under a wide range of flow conditions. Several tributaries, however, were found to have relatively high nutrient concentrations, particularly those associated with agricultural land uses or large fish farms, and those originating in limestone terrain. Extensive data were collected over a two-year period at the lowermost site (Bryn Estyn)—as summarised in Table 1. Nitrate-nitrogen showed a strong seasonal trend (high in winter, low in summer), paralleled by total nitrogen values.

Table 1. Nutrient levels (μg/L) in the Derwent River at Bryn Estyn, Tasmania

	NO_x	NH_3	PO_4	TP	TN
N	259	249	260	259	259
Mean	25	8	2	9	234
Minimum	4	2	2	2	118
Maximum	58	62	3	41	696
Std dev	11	8	0.1	6	82

Nutrients in the Derwent estuary

Nutrient concentrations in the Derwent estuary were initially monitored over a one-year period, commencing in March 1993 (Coughanowr 1995, 1997). Water samples were collected fortnightly at 51 stations, at the surface and at depth. Considerable variability was observed, both seasonally and spatially. Nitrate+nitrite levels during the study period averaged 14 μg N/L for surface samples and 16 μg N/L at depth, with generally higher levels (15–30 μg N/L) observed in the upper estuary, reflecting river inputs. Nitrate–nitrite concentrations were seasonally elevated at the estuary's mouth (May through July), because of oceanic inputs. Ammonia concentrations averaged 20 μg N/L in surface waters and 25 μg N/L at depth, with the highest ammonia levels (100–200 μg N/L) observed at depth in the middle and lower estuary. Orthophosphate levels in the estuary averaged 6 μg P/L in surface waters and 9 μg P/L at depth, with slightly higher values observed in the middle estuary.

In 1996, this survey was followed up by a co-ordinated program between DPIWE and Fletcher Challenge Paper (FCP) which included measurement of the full range of nutrients plus chlorophyll *a* (26 sites surveyed at six-weekly intervals). Ammonia-N, orthophosphate and total phosphorus concentrations showed similar magnitudes and trends to values observed in the Derwent Estuary Nutrient Program (DENP), with higher mean concentrations in middle reaches of the estuary, particularly in embayments. Nitrate-N concentrations were significantly higher (nearly double) those observed in DENP, probably reflecting elevated oceanic concentrations in May–July. Total N concentrations (which had not been monitored in DENP) showed a progressive increase with distance up estuary, with mean concentrations ranging from 110 µg/L at the mouth to a maximum of 310 µg/L near FCP-Boyer, falling to 240 µg/L in the river at New Norfolk.

Chlorophyll a *and macro-algae*

Data on chlorophyll *a* concentrations in the Derwent estuary (1996) showed considerable variability with chlorophyll *a* concentrations ranging from less than 0.5 µg/L to a maximum of 24 µg/L in Prince of Wales Bay. In general, the highest mean concentrations of chlorophyll *a* were observed in the middle estuary, and particularly in embayments such as Prince of Wales Bay and New Town Bay. The upper reaches of the estuary were consistently low in chlorophyll *a*, while the lower estuary and nearshore coastal waters occasionally had high concentrations.

No quantitative data on the distribution or biomass of macro-algae are available for the Derwent, although there have been some reports of nuisance growth in certain embayments (eg. Cornelian Bay). Seagrass beds at the mouth of the Jordan River show variable degrees of epiphytic algal growth.

Nutrient/algal dynamics

The relationship between nutrients and algal growth in the Derwent estuary is not well understood. The Derwent may not be highly susceptible to algal problems, because of a number of physical characteristics of the estuary; particularly the relatively low water temperatures and short water residence time. Furthermore, the estuary has been described as having poor light penetration, because of the naturally highly coloured, humic-rich waters discharged by the Derwent River. Measurements of euphotic depths in the upper estuary are typically in the order of 4 to 10 m (Richardson, 1998), while Secchi depth measurements in the middle and lower estuary are almost always greater than 2 m and often considerably higher (DPIWE, unpublished data).

On the basis of several years of monitoring data, it appears that significant concentrations of bioavailable nutrients (PO_4, NH_4, NO_3) are present in the water column throughout the year. This appears to be largely a natural phenomenon, caused by inputs of nutrient-rich Southern Ocean water—particularly during winter and spring—although there is some further nutrient enrichment of the mid-estuary from sewage inputs. This enrichment of bioavailable nutrients does not appear to occur, however, in the upper estuary and Derwent River, where orthophosphate concentrations are consistently below detectable levels (less than 2 µg/L).

It is something of a puzzle as to why phytoplankton in the middle and lower estuary do not appear to be responding to the availability of nutrients. It is possible that phytoplankton are flushed from the estuary before reaching their maximum standing crop. Alternatively, another factor may be limiting phytoplankton growth, for example:

- low water temperatures (depresses growth rates);
- light limitation (high colour reduces light penetration, limiting rate of photosynthesis and algal productivity);
- presence of dissolved organic compounds (eg. humic and fulvic acids, which may interfere with nutrient availability/uptake and/or exert toxic effects);
- some toxin (eg. heavy metals) or group of toxins, which could depress phytoplankton growth;
- absence or limitation of some other essential element; and
- grazing controls by zooplankton.

Threats

Both the Derwent River and the Derwent estuary appear to have significant concentrations of bioavailable nitrogen at most times. Bioavailable phosphorus is also seemingly plentiful in the middle and lower estuary, but very limited in the upper estuary and river. Nitrogen sources include both anthropogenic inputs (particularly from sewage treatment plants and fish hatcheries) and natural, seasonal inputs both from the catchment and the ocean. Problems with recurrent nuisance algal blooms have not been evident to date and the potential for future problems is unknown. Changes in effluent treatment at a large pulp mill at the head of the estuary could potentially alter nutrient dynamics in the estuary; this is currently being investigated as part of a detailed ecological risk assessment of the upper estuary.

Management actions

To date, management actions have focused on nutrient monitoring, reporting and the prevention of further increases. Improvements to sewage treatment plants have resulted in a reduction in nutrient discharges to the estuary by approximately 5–10% in the past three years. On-going and planned improvements in fish hatcheries in the upper catchment should also reduce nutrient discharges to the river.

Information gaps and needs

- Given the relatively elevated concentrations of nutrients in the Derwent estuary, why don’t we experience algal blooms?
- Is the Derwent susceptible to nutrient-induced algal problems? Under what conditions?

- Is ‘holding the line’ an acceptable management strategy, or do we really need to know what makes the system tick?
- Are reported historical seagrass losses linked to elevated nutrient concentrations? If so, how much should we reduce nutrients to encourage re-establishment of these beds?
- How can monitoring programs, process studies and predictive modelling be brought into the realm of the affordable?

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The West Australian experience with nitrogen: a review, opinions and identification of needs for better waterways management

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Introduction and background

The legacy of phosphorus

In contrast to the northern hemisphere where considerable research has studied the sources and sinks of nitrogen (N) in catchments and inland waters, waterway managers in Western Australia (WA) have traditionally focused on the control of phosphorus (P). In WA we have a history of dealing with this important nutrient for over 20 years. This P-centric management attitude had its origin in the late 1970s with the Peel–Harvey estuarine experience. Research at the time identified phosphorus as the cause of the blue–green *Nodularia* blooms and its control as the solution. The Peel–Harvey experience influenced the approach taken to water quality management in WA for the next 30 years. The P problem on the coastal plains of the south-west was linked to excessive over-clearing and fertiliser applications on leaching sandy soils with poor phosphorus retention properties. Some work in the late 1980s pioneered identification of N pathways (on the Darling Scarp) and provided explanations for the lower than expected N levels under some sandy coastal soils (eg. Turner and Macpherson, 1990; Gerritse et al., 1990). In general the significance of this work was not widely appreciated by management until recently.

Changing appreciation for nitrogen

Environmental managers in WA have now realized the importance of other limiting nutrients to phytoplankton productivity. To manage eutrophication, the strategy is now one of coupled reductions in both P and N. While the various transformations and transport pathways of N, role of microbes and their micro-environments and the role of oxygen and pH are only superficially understood in WA, there is a growing body of knowledge about N in the context of agricultural activities like horticulture and broad acre production (eg. Lantzke, 1999).

We are slowly gaining a better understanding of the mobility of nitrates and other species of N under conditions of waterlogging and shallow groundwater levels that are common on the coastal plains of the south-west. Better advice on N fertilisers is becoming available (Angel, 1998). Perhaps though, a turning point for estuarine managers was a recent study on the critical role N limitation has on phytoplankton productivity in the Swan–Canning Estuary (Thompson and Hosja, 1996). We are getting a better appreciation of how it moves through the urban landscape (Gerritse et al., 1990; Appleyard, 1992; Paice, 1999). Nevertheless, practical management advice and applications to help reduce or eliminate N availability in the catchment and its transportation to inland waters and estuaries are still lacking. Fundamental ignorance in N cycling remains regarding sources and sinks in variety of environments, nutrient fluxes, and the scale of exchange between transformation stages.

The setting

The southern half of Western Australia has a Mediterranean climate with wet winters and dry, hot summers. Rivers, wetlands and waterways are mainly seasonal, usually flowing or wet during winter and spring, and drying out for the rest of the year. Inland drainage systems are often river channel pools that occasionally flow rather than *proper* river systems containing water that flows to the ocean in meandering *blue ribbons*. Shallow groundwater levels are common on the sandy coastal plains and seasonal waterlogging caused by rainfall and elevated groundwater tables affects much of the coast. Inland soils are generally lateritic and have more complex geologies that predispose them to variable groundwater levels and greater problems with salinisation. The topography is low relief and much of the south-west coast is microtidally affected, changes in barometric pressure driving the biggest changes in water levels and affecting marine and estuarine exchange.

Ground and surface waters along the south-west coast are thought to be naturally high in organic N but low in

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inorganic N. Natural vegetation is dry sclerophyll woodland but most of this has been cleared for grazing (sheep and cattle) and cereal cropping, mostly between 1940 and 1980. Clover-based pastures are extensive. Pastures are generally fertilised before winter rains in the belief that this will promote the establishment of plants and their good growth in spring. The replacement of deep-rooted vegetation by seasonal, shallow-rooted crops has reduced evaporation, increased surface run-off and groundwater recharge. This has, in turn, increased annual flows in many coastal south-west rivers.

Waterways and estuaries in the south-west have been reasonably well studied in comparison to those in the mid and tropical northern latitudes of the State. The catchments, tributaries and estuaries of the Swan–Canning, Peel–Harvey, Leschenault, Hardy, Wilson and Princess Royal Harbour and other Albany waterways are probably the best known. Many of the streams feeding into these systems are groundwater driven, particularly for coastal catchments. Nutrient budgets, processes and fluxes for these systems are less well studied but some information is available. The link between N and algal blooms is strong but mainly correlative and not causative. We have little detailed understanding of N transformations once it is flushed into aquatic systems, or of the temporal and spatial response of phytoplankton and other biota to these inputs.

What we know

Role of water

Nitrogen, mainly as nitrate, is readily soluble in water and is rapidly transported through the catchment via surface run-off, and sub-surface (including sub-surface storm flows from duplex sands over clays) and groundwater flows. In very wet periods, all pathways can be actively discharging N to stream channels. In dry periods, groundwater is the main long-term component of flow and is the only source of N to streams. Water is thus central to the mobility of N. When dry soils become wet they lose nitrates; where there is no water loss there is no leaching of N from catchments. We are certain of the critical status of groundwater and surface and sub-surface run-off in the transport of N on the coastal plain. We also know that, in wet winters, a large proportion of total organic N entering from strong river flows is flushed out to the ocean in the Swan–Canning Estuary (Fredericks et al., 1998).

Point and diffuse sources

In WA we know, in general, where the large majority of point sources are located but have a poor understanding of what they contribute or their loads to the environment. Some are licensed, although a number are not well managed because of political and departmental enforcement difficulties. Point sources on the Swan coastal plain include landfill sites, contaminated sites, commercial and industrial operations, and intensive livestock areas. Very high ammonia and nitrate concentrations have been recorded near intensive poultry and pig farming localities and the disposal of their associated liquid wastes. Septic tanks in urban areas are important sources of concentrated N that is mobilised primarily by groundwater (Gerritse et al., 1990).

Diffuse sources of N largely originate from rural practices including fertilised arable lands, pasture, orchards and intensive horticulture practices where fertiliser application is excessive and groundwater levels are high (Gerritse, 1992; Lantzke, 1999). In urban areas, appreciable quantities of fertilisers are applied to parks, gardens and sports grounds. It has been estimated that fertilisers applied to urban gardens account for approximately 10% of total nutrient inputs to the Swan–Canning Estuary (SCCP, 1999).

Inputs of N

Locally high nitrate concentrations (~20 mg/L) have been found in the superficial aquifers of the urbanised and agricultural areas in the Perth region and are related to overuse of fertilisers, as well as leachate from septic tanks (Davidson, 1995). Extremely high nitrate concentrations (sometimes greater than 60 mg/L) have been associated with horticultural and recreational areas (eg. sports grounds). Leaching of nitrate to groundwater is significant in the sandy areas, especially in the coastal Spearwood Sands and to a lesser extent in the Bassendean Sands that have more favourable conditions for denitrification (Gerritse et al., 1990). The high applications to the land surface but low concentrations in groundwater nearby are thought to be caused by high rates of de-nitrification in the soils of the coastal plain. The naturally high concentration of dissolved organic carbon in the Bassendean Sand aquifers, and a pH between 5 and 7, is ideal for microbial denitrification and is probably responsible for the loss of significant amounts of N from coastal plain catchments (Gerritse et al., 1990). However, there are reasons to believe that current nitrate concentrations in groundwater may not be at equilibrium and may increase in the future (Davidson, 1995).

It is believed that native vegetation with a large proportion of N-fixing species combined with clover-based pastures also make important contributions to N levels in south-west streams, particularly when lowland bush areas and paddocks become saturated.

Catchment specific information with application to inland areas

The dominant pathway for nitrate leaching from Darling Plateau catchments is surface run-off and sub-surface storm flow (Turner and Macpherson, 1990). Most of the nitrate is leached during the first major rainstorms of winter (sometimes >20 mg/L nitrate), after which nitrate concentration rapidly decreases. Nitrate concentrations are typically less than 1.0 mg/L in the shallow perched groundwater and less than 0.1 mg/L in deep groundwater. The low concentrations suggest groundwater is not a major pathway for N to tributaries from the Darling Plateau (Turner et al., 1991). The Darling Scarp has more similar sediment characteristics to inland wheat belt areas than the coastal plain and thus N transport and nutrient levels described there may be indicative of inland conditions.

Role of N in estuaries, inland waters and poor water quality events

We have better information on N for estuarine environments than for most inland waters but even this is limited. Thompson and Hosja (1996) showed that N was limiting for phytoplankton growth during late spring and summer in the Swan–Canning Estuary. This was the first rigorous work to reveal the critical role N limitation played in the water quality of this urbanised estuary. Monitoring for the SCCP Action Plan has revealed that most estuarine N is incorporated into phytoplankton cells and that N release (often as ammonium) from sediments is common during summer. Some research in N cycling in inland waters has occurred but generally has not reached management or influenced its thinking.

Table 1. Typical nitrogen (TN) concentrations (mg/L) based on 80%ile data in unmodified streams (uncleared catchments) compared with modified streams (cleared and agricultural catchments). Note the naturally high background levels of TN in modified lowland coastal streams.

		TN	NO_x	NH_3
Upland	unmodified	0.45	0.2	0.06
	modified	1.30	0.36	0.12
Lowland	unmodified	1.2	0.15	0.08
	modified	2.70	0.45	0.17
Urban	modified	2.5	0.60	0.75

What we don’t know

Interpreting land-use changes through monitoring signals and temporal trends

There have been very few attempts in Western Australia to characterise the types of nutrient trends that can be expected in catchments subject to changes in land use. In most catchments we do not know the time-lag between control and expression of the improvement in waterways. We don’t know what statistical changes characterise a reduction or increase in point sources or improvements in diffuse sources ie. monotonic or step increases or declines in trend.

We do know that the economic, agricultural wealth of the State is dependent on the use of fertilisers on the naturally poor soils of WA. We also know that the current rate of use is not sustainable if natural values of aquatic environments in WA are to be protected. We can only guess at the ecologically sustainable level of N (or P) use and how to achieve it.

The fate of N

Some overseas work suggests that as little as 20% of N added to sandy catchments may reach the estuary (Valiela et al., 1997). However, in WA we don’t know how much reaches our estuaries from point and diffuse sources, let alone how much is processed and lost to the atmosphere before reaching estuaries.

Sources of N

Diffuse sources of N are assumed to be mainly associated with poor urban and rural fertiliser and land-use practices and from poor light industry practices. However, it is unknown what the role and contribution of weathering and atmospheric deposition is to N inputs to aquatic systems. We have assumed they are negligible.

Role of riparian vegetation

We are uncertain what role and scale of influence riparian vegetation plays in cycling N. We also need to know what vegetation suites are most effective in a variety of conditions to enhance N processing and denitrification. Such information would greatly assist the development and implementation of rural and urban best practices.

Understanding fine temporal scales of N transformation

Currently in WA when a rain event occurs between spring and autumn and substantial run-off enters open aquatic systems, a phytoplankton bloom is likely to follow within two to three weeks. This has been observed repeatedly in WA estuarine and weir pool environments. Understanding the short-term transformations and fluxes of N transfer may help us to better manage water quality particularly in an interventionist sense eg. utilising oxygenation, sediment remediation techniques or modifying transformations, processing stages and biological sinks.

Use of applied models for better understanding of N

There is a plethora of N models to use on both rural and urban catchments (eg. Whelan et al. 1995) as well as to help understand N processing in aquatic environments.

Almost all of these were developed in the northern hemisphere. However, having a more restricted list with models appropriate for a variety of Australian conditions would help immensely in the management of N. Such a critique and reference could help agencies and managers to more quickly and efficiently learn about N management. Basically, we lack region-specific and helpful N catchment models, particularly those that link processes to land-use changes which in turn are linked to nutrient exports.

Basic research on N interactions between land–soil–groundwater–waterways–estuaries

To help identify the level of sustainable N use, basic research on processes, interactions and connections between the various interfaces of the environment is still needed for many WA environments. We still need applied information on the scale of N fluxes, processes, links, sources and sinks.

Management

In WA a number of environmental plans have recently been implemented at the catchment-scale. The five year $14 million Swan–Canning Cleanup Program (SCCP) Action Plan (1999) for the coastal plain portion of the Swan–Avon and Canning Rivers targets N as well as P reduction to improve water quality. For the plan to work it needs better information on N management. Complementing the requirement for N reduction is a compliance system with target N levels. This has helped raise the profile and importance of managing N as well as P. A supporting statutory Swan–Canning Environmental Protection Policy (1998) by the WA Department of Environment has also been gazetted which enshrines the use of a N compliance and target system. A similar need exists for the Peel–Harvey system where N management has been traditionally ignored.

The SCCP *Action Plan* and a Coast and Clean Seas grant are directly funding the construction of an artificial wetland and modifications to an urban drainage system to enhance N processing and removal. The SCCP *Action Plan* encourages the use of constructed wetlands to reduce N inputs to the Swan–Canning Estuary.

Recent work by Lantzke (1999) has helped develop codes of practices for the horticultural industries. These codes have provisions for N management, particularly for reducing nitrate losses to groundwater.

Needs

Western Australia needs information on how to:

- maximise N uptake by plants, crops and riparian vegetation. This information would assist in the development and improvement of technical best management practices and restoration efforts, particularly for agriculture and semi-rural scenes. Related to this is a need for better understanding of the role for micronutrients in improving N uptake in plants. Emphasis in WA has been on ‘streamlining’, fencing and restoration of riparian vegetation assuming this will naturally enhance N processing.
- develop smart *shake and bake* techniques (microbial dosing or localised micro-landscaping recipes) that can enhance microbiology and microenvironments for N processes. For example, nitrifiers are a restricted and environmentally sensitive suite of organisms (compared to ammonifiers often leading to NH_4^+ accumulation). It may be possible to identify and inoculate areas with a hardy and quickly populating endemic species. Any chance of microbially enhancing N processing zones in paddocks? We are also ignorant of the fate of N in groundwater and the subsoil just below the surface. Are any biological and chemical transformations susceptible to management to reduce eventual groundwater contamination and discharge?
- elaborate on the contributions of various processes to nutrient export and also the distribution of those processes across and under the generic catchment as defined by different topographies and geology.
- better identify the sources of N, particularly diffuse sources.
- identify the best N models to use (most likely in conjunction with catchment models) that will assist in decision making and management.
- have a better *applied* understanding of N cycling within aquatic environments, particularly in wetlands, river pools, seasonal streams and estuaries.

Most importantly, we need to identify ecologically sustainable levels of N use. We know current levels are unsustainable. We need to formulate strategies to reduce N loss from catchments that enter estuaries. This is paramount in light of growing evidence that south-western estuaries are seasonally N limited (eg. during summer) and possibly N limited for significantly longer periods of time (ie. mid spring to mid autumn).

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The atmospheric nitrogen cycle over Australia

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Abstract

The processes regulating the cycle of fixed nitrogen (N) through the atmosphere are reviewed and the available information on the processes over continental Australia is presented. The major sources that contribute to atmospheric fixed N are soil microbial processes, animal excreta, biomass burning, fossil fuel consumption and lightning. The major sink processes returning fixed N from the atmosphere to the terrestrial biosphere are wet and dry deposition. The average rate of emission of fixed N over Australia is of the order of 3 kg N ha^{-1} y^{-1} and the observed deposition rates in different environments are: oceanic 0.3 kg N ha^{-1} y^{-1}; remote rural 2 kg N ha^{-1} y^{-1}; rural with major coal fired utilities 4 kg N ha^{-1} y^{-1}; and urban regions 11 kg N ha^{-1} y^{-1}. Current research issues and activities concerning the atmospheric N cycle over Australia are presented.

Introduction

For the atmospheric sciences, the biosphere is a crucial lower boundary. It is a source of many of the inputs into the atmosphere that drive the atmospheric chemistry, and it is a sink for the removal of many species from the atmosphere. While for some nitrogen (N) species the biosphere acts as both a source and a sink, for others the boundary is predominantly one or the other, and the atmosphere is the reactor that converts N species that predominantly originate in the biosphere into other N species that are deposited back to the surface. The atmosphere is a small reservoir for reactive N species in comparison to the biosphere. While N deposition to the earth's surface constitutes a significant pathway of fixed N loss from the atmosphere, in the context of N cycling within the terrestrial biosphere this deposition is generally a minor flux. There are exceptions, notably in regions where there is intense, normally acidic, deposition of oxidised N species arising from industrial emissions, such as have prompted extensive research and monitoring programs in the USA, Canada and northern Europe, and to a lesser extent in Asia and the tropics.

The subject of atmospheric N cycling in the Australian context has been reviewed by Galbally and Gillett (1988) and Galbally et al. (1992). These papers give a good overview of the underlying principles. Work in the field has continued steadily with sufficient developments, particularly in the experimental data, to justify another comprehensive review. However, there have been no revolutionary developments in the science, that invalidate the views previously expressed.

The atmospheric nitrogen cycle

Sources and atmospheric transformations of nitrogen species

The atmospheric N species of particular relevance to the biosphere/atmospheric exchange are (by increasing oxidation state) NH_4^+, NH_3, nitriles, N_2O, NO, NO_2, organic nitrates, NO_3^-, and HNO_3. Most of these species are reactive and therefore have atmospheric lifetimes ranging from a few days to two weeks (Table 1).

Table 1. Key atmospheric nitrogen species and typical atmospheric lifetimes

Species	Lifetime	Ambient concentration
NH_4^+	1–2 weeks	0.02–5 ppbm
NH_3	1–7 days	0.1–20 ppbv
N_2	10^5 years	78%
N_2O	120 years	310–350 ppbv
NO, NO_2	1–2 weeks	0.01–1000ppb
Alkyl nitrates, PAN	1–2 days	0–1 ppbv
NO_3^-	1–2 weeks	0.04–1 ppbm
HNO_3	1–2 weeks	0.1–1 ppbv

The exception is N_2O which has attracted particular attention in the past decade because it is a potent greenhouse gas and photodecomposes in the stratosphere to provide a source of nitric oxide, which in turn regulates stratospheric ozone chemistry. The acidic and basic N species have been the subject of particular investigation because of their role in urban and regional pollution through (1) acid deposition and soil acidification and (2) photochemistry leading to photochemical smog (Seinfeld and Pandis, 1998).

Fixed N compounds are released into the atmosphere from various sources including:

1. Microbial processes in the soil, principally nitrification and denitrification that produce both NO and N_2O as loosely coupled intermediates that then diffuse through the soil to the atmosphere. The N substrates required for these transformations derive from:
   - the mineralisation of organic N from decomposed litter etc.;
   - mineralisation of animal faecal waste particularly from agricultural animal production;
   - animal urine;
   - inorganic fertilisers applied to crops and pastures; and
   - deposition of atmospheric N compounds.
2. Microbial digestion of urban and agricultural organic waste in waste and sewage treatment plants that release NH_3, N_2O and NO.
3. Composting of manure and agricultural residues that emit NH_3, amines, N_2O and NO.
4. Application to crops and pastures of artificial fertilisers and animal urine that hydrolyse to NH_3, and that in turn can volatilise. These fertilisers include urea, ammonium fertilisers and anhydrous ammonia.
5. Industrial combustion (ie. high temperature) processes that catalyse the reaction of molecular N with oxygen to produce NO. Some industrial plants are fitted with catalytic NO and NO_2 scrubbers that substantially reduce NO emissions but produce N_2O as a by-product. These sources include:
   - coal-, gas- or oil-fired electricity generating plants;
   - furnaces and stationary engines involved in industrial production; and
   - transport (cars, commercial vehicles, rail, air and shipping).
6. Biomass combustion (ie. low temperature) processes including (i) fires in savanna woodlands and temperate grasslands, (ii) prescribed fires in forests, both fuel reduction and regeneration burns (iii) wildfires, (iv) burning of agricultural crop residues and (v) domestic wood fires. These processes release NH_3, NO and NO_2, organic nitriles, amines and cyanides.
7. Some chemical production processes release N compounds directly to the atmosphere. For example, the synthesis of adipic acid for nylon manufacture is a significant source of N_2O in some countries, but in Australia these direct sources are mostly insignificant. There are some minor emissions associated with the manufacture of nitric acid and ammonia for industrial chemical processes and inorganic fertiliser production. These emit NO, N_2O and NH_3.
8. Additionally, NO can be produced directly in the atmosphere from molecular N through lightning strikes.

Emission rates of nitrogen species into the atmosphere

NO_x emission

The N oxides (NO_x) are both criteria pollutants and indirect greenhouse gases, and as such are included in both pollution and greenhouse gas inventories. These inventories are valuable resources of knowledge about the anthropogenic component of the continental emissions. The natural emissions are more poorly understood and are more difficult to quantify. There have been very few Australian studies of the natural source of NO emission from soil in natural and rural systems (however, see Galbally and Roy, 1978; Galbally et al., 1985; Galbally et al., 1987). Emission rates from temperate pastures are of the order of 3 ng N m^{-2} s^{-1}, however emissions from cropped soils, particularly crop/legume rotations are frequently much higher (Duffy et al., 1988).

Estimates of the annual Australian emissions of NO_x are presented in Table 2. The natural emissions are estimated from previously discussed measurements of NO fluxes from soil and the anthropogenic components are derived from the National Greenhouse Gas Inventory for 1997 (NGGIC, 1999). Soil emissions contribute approximately half the total emission of 1700 Gg N; fossil fuel combustion contributes 26%, lightning around 8% and biomass burning in forests and savanna contributes approximately 17%. The magnitude of the sources of NO_x in the Australian context are estimated using the 1996 Revised IPCC Guidelines for Greenhouse Gas Inventories (IPCC, 1996). This methodology is a useful, and internationally agreed, approach to quantifying emissions and provides the basis for the national greenhouse gas inventory methodologies of most countries.

NH_3 emission

Ammonia volatilisation is also an extremely important mechanism for lots of biospheric fixed N and is a major pathway for loss of N applied as urea and ammonia-based N fertiliser, deposited by grazing animals, or animal waste management. Gaseous losses of inorganic fertiliser

N can be very large, typically 50% and exceeding 70% under some cropping regimes eg. sugarcane (Weier et al., 1996). While some of this fraction is due to denitrification (as NO, N_2O and principally N_2), NH_3 volatilisation is thought to account for significant fraction of the total N applied; particularly for urea where 10% to 20% of applied N is emitted as NH_3 (Galbally et al., 1987; Pain et al., 1998; Van Der Hoek, 1998). Emission of NH_3 from faecal and urine deposition by grazing animals is a second, and largely uncontrollable source, of atmospheric NH_3.. Volatilisation from urine patches can account for the order of 25% of urine N deposited, while approximately 10% of faecal N can be emitted as ammonia. McLaughlin et al. (1992) give a good overview of NH_3 cycling for Australia.

Ammonia volatilisation, transport and deposition is a major environmental question in the northern hemisphere, particularly in western Europe and has lead to several large scale international programs aimed at quantifying regional ammonia budgets (eg. Sutton et al., 1998).

Under the IPCC Inventory Guidelines (IPCC, 1996), NH_3 emissions are calculated as indirect sources of N_2O; indirect, because they are in part converted to N_2O through the cycle of volatilisation, atmospheric transport, deposition and subsequent denitrification in soil. The IPPC methodology recommends the assumption that 10% of fertiliser N and 20% of N excreted by livestock is volatilised. If so, in 1997, 75 Gg of fertiliser N and 475 Gg of N excreted by grazing animals, ie. 550 Gg N, was emitted into the atmosphere from agriculture in Australia, the majority as NH_3.

Biomass burning is also a significant source of ammonia (Andreae et al., 1996), with between 4 and 23% of plant N emitted as this species during combustion (Hurst et al., 1996; Andreae et al., 1996). Assuming an emission factor of 11% for savanna fires and 17% for forest fires then total emission from this source in Australia in 1997 was approximately 150 Gg N (Table 3).

Other nitrogen species

Amines, nitriles and organic nitrates and cyanides are emitted principally from biomass burning, the majority

Table 2. Estimated source strengths for NO_x and NH_3 in Australia

Sector	NO_x emission (Gg N)		NH_3 emission (Gg N)[d]	
Natural ecosystems[a]	800		?	
Crops and pastures[a]	65		485	
Lightning[c]	140		?	
		1005		*485+*
Biomass combustion				
Savanna and grassland fires[b]	270		142	
Prescribed burning of forests[b]	3		3	
Wildfires in forests[b]	10		10	
Agricultural waste burning[b]	5		?	
		298		*155+*
Fossil fuel combustion				
Energy production[b]	160		?	
Transport[b]	140		?	
Industrial processes[b]	120		?	
Agriculture, commercial, domestic[b]	30		?	
		450		?
Total		**1753**		**640+**

[a] Galbally et al. (1992)
[b] NGGIC (1999)
[c] Galbally and Gillett (1988)
d The emissions of ammonia from several major sources in Australia have not been quantified to date. They are identified by '?', and the subtotals which include these sources are therefore lower bounds of the actual ammonia emissions.

from fires in the savanna woodlands of northern Australia. Using the emission factors reported by Hurst et al. (1994,1996) and Andreae et al. (1996) the total emission of these other N species from Australia in 1997 was of the order of 380 Gg N (Table 3).

In total, the annual emission of fixed N into the troposphere over Australia is in the order of 2700 Gg N. Averaged across the area of Australia, this corresponds to an average emission rate of approximately 3 kg ha^{-1} y^{-1}.

Table 3. Emission of nitrogen species by biomass burning

Species	Emission (Gg N)		
	Savanna fires	Prescribed fires	Wildfires
NO_x	270	3	10
NH_3	142	3	10
NO_y (nitrates and HNO_3)	330	5	15
Acetonitrile	26	0.4	1.2
Cyanide	7	0.1	0.3

Atmospheric concentrations and transformations

The atmospheric lifetimes and concentrations of key N species are presented in Table 1.

Once in the atmosphere fixed N species are subject to a large set of chemical transformations. These reactions convert otherwise stable species into compounds that react rapidly with vegetation and soil surfaces, or are soluble aerosols that can be rapidly and efficiently removed from the atmosphere by rainfall.

N_2O is highly stable with a lifetime of the order of 100 years. Within the stratosphere N_2O is photodissociated to N_2, and O, and reacts with excited atomic oxygen to produce NO.

The NO_x (ie. NO plus NO_2) concentration in clean southern hemisphere marine air is around 0.03 ppb with NO ranging from 0 to 0.01 ppb and NO_2 concentration from 0.01 to 0.03 ppb (Galbally et al., 1999). In rural air the NO_x concentrations are higher, ranging from 0.01 to 2 ppb (Galbally et al., 1987). An example of ambient NO_x concentrations at Cape Grim that receives both clean marine air and air from the rural forested regions of north-west Tasmania is shown in Figure 1 (Galbally et al., 1999). The mean NO_x concentration for November/ December 1995 was 0.065 ppb NO_x ranging from 0.008 to 1.1 ppb. Mostly the NO_x was present as NO_2 (85%) ranging from 40% to 100% depending on the time of day and the source of the air mass. In more landlocked rural environments the NO_x concentrations are higher, (1 to 2 ppb), but in urban airsheds, particularly in the vicinity of major roads the NO_x concentrations can approach 1 ppm, see Table 4. At very high NO_x concentrations relatively little of the NO emitted is converted to NO_2 and therefore NO_2 concentrations rarely exceed 100 ppb.

NO is a pivotal species in ozone photochemistry in both the troposphere and the stratosphere: it is rapidly converted to NO_2 by reaction with ozone, while NO_2 is photolysed to NO (Seinfeld and Pandis, 1998). In addition both species are active in an extensive free radical chemistry. The two species NO and NO_2 rapidly interchange in the atmosphere due to these chemical reactions, hence they are collectively described as NO_x. Nitrogen dioxide is further oxidised to nitric acid (HNO_3). Ammonia and amines are subject to attack by the hydroxyl radical. They also react with nitric acid to produce nitrate salts (in the case of NH_3 to produce NH_4NO_3), most of which exists in the atmosphere as aerosol. Nitriles are also thought principally to react with hydroxyl radicals ultimately forming cyanide radicals. Nitrites and some nitrates (eg. PAN) are destroyed by photolysis.

Many of the atmospheric N species, particularly NO_2, NH_3, NH_4NO_3 and other nitrate aerosol, return to the surface either by uptake by plants and soil (dry deposition), or by removal in solution by rain (wet deposition). Overall, in the troposphere, very little of the fixed N emitted into the atmosphere from the biosphere is converted to molecular N. If we ignore tropospheric/ stratospheric exchange, it is reasonable to say, with respect to fixed N compounds, that what goes up must come down.

Removal of nitrogen from the atmosphere by deposition to the surface

Nitrogen is removed from the atmosphere by two pathways: dry and wet deposition.

Table 4. Typical NOx concentrations at Doncaster, Melbourne

Month	NO (ppb)[1]		NO_2(ppb)[a]		Percentage NO_x as NO_2
March 1999	24	(0–470)	13	(0–52)	55
August 1999	55	0–740)	19	(4–58)	47

[1] Mean and range

Dry deposition consists of the transfer of N species from the atmospheric boundary layer to crop and soil surfaces via turbulent and diffusive transport. The deposition rate is generally determined from the trace gas concentration in the air at a fixed height above the surface (typically 2 m or 10 m) and the deposition velocity, which is a function of the physical and biological characteristics of vegetation and soil.

NO_x is deposited to the surface principally as NO_2, which is rapidly absorbed by leaves and soil, and has no significant soil source. NO is both produced and consumed by soil (Johansson and Galbally, 1984; Galbally and Johansson, 1989), but the uptake rates of NO by plants are typically small. The NO compensation point at the soil surface varies with soil properties, particularly soil moisture, and can range from about 1 ppb to more than 150 ppb, and therefore, depending on the atmospheric NO concentration, the soil can be either a net source or a net sink. At high NO concentrations, net NO deposition will occur in addition to NO_2 deposition, although NO deposition rate is typically about 20% of that for NO_2 (Galbally et al., 1985; Seinfeld and Pandis, 1998; Neubert et al., 1993).

Ammonia is efficiently deposited by dry deposition. Ammonia is metabolised by plant leaves and is subject to stomatal regulation and therefore the deposition velocity has a strong diurnal dependence. Deposition is particularly rapid over dense vegetation particularly dense crops and forest. In consequence a large proportion of ammonia is deposited within a few kilometres of the point of emission; in some circumstances up to 60% may be deposited within 2 km of the point of emission (Asman, 1998).

Wet deposition occurs by the scavenging of gaseous and aerosol forms of fixed N species by water droplets in clouds, mist and rainfall. The process is extremely efficient at removing some species from the atmosphere with washout efficiencies approaching 100%. However, while dry deposition occurs continuously, wet deposition is proportional to both atmospheric concentration and total rainfall.

Some measurements of wet deposition have been made in studies of forest nutrient cycles giving a mean value for south-eastern Australian forests of 5 kg N $ha^{-1}y^{-1}$ (Attiwill et al., 1996). However most of the more recent measurements of wet and dry deposition have been made in projects addressing both broad issues of atmospheric chemistry in urban and in unpolluted environments, and projects commissioned to assess the impact of acid deposition resulting from industrial air pollution. The current Australian data available in the open literature from these studies (Ayers and Gras, 1983; Ivey et al., 1996; Gillett, 1998) are summarised in Table 5. The locations have been grouped into (i) oceanic atmospheres, (ii) remote rural atmospheres, (iii) rural airsheds that contain major coal-fired electricity generators, and (iv) urban atmospheres.

Since the studies were not designed to measure regional trace gas budgets, there are no cases where the deposition of all major N species were measured. It is of note that there are no direct measurements for N deposition in the Melbourne airshed: the deposition rates were estimated for the Port Phillip Bay Environmental Study from a literature survey (Carnovale et al., 1992), which is a significant gap in environmental baseline data for the second largest city in Australia. The available data are combined together to provide estimates of N deposition in various regions of Australia. The total N deposition rates vary from about 0.3 kg N ha^{-1} y^{-1} in oceanic areas to approximately 2 kg N ha^{-1} y^{-1} in remote rural and natural regions, ~5 kg N ha^{-1} y^{-1} in airsheds containing

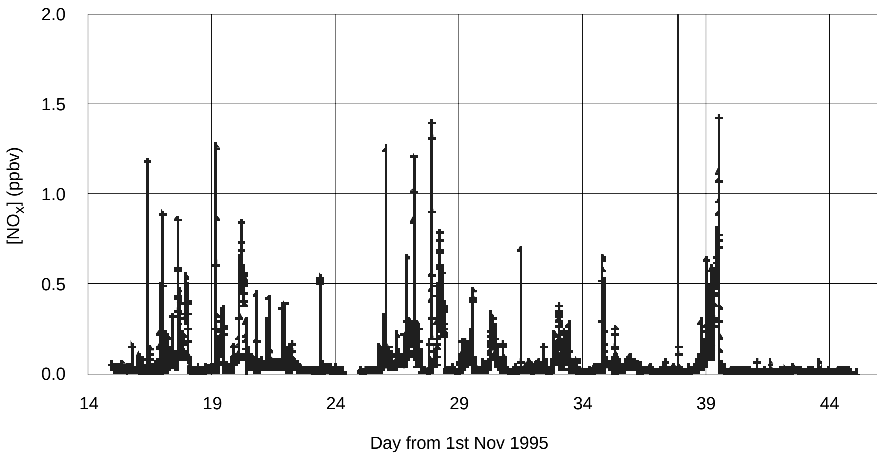

Figure 1. Ambient NO_x concentrations at Cape Grim, Tasmania, November–December 1995. Mean marine air concentration: 0.019 ppbv. Mean concentration all windsectors: 0.065 ppbv

coal-fired power utilities and approximately 10 kg N ha^{-1} y^{-1}in urban areas (Table 6). Dry deposition predominates in the rural airsheds surrounding power stations due to the large amounts of NO_x emitted, while in the oceanic/coastal regions, wet deposition accounts for the major fraction of N losses from the atmosphere. In natural, rural and urban airsheds dry and wet deposition rates are similar. These estimates of deposition match well the Australia-wide average emission of approximately 3 kg ha^{-1} y^{-1}.

Another form of N deposition in agroecosystems is fertiliser addition. While some areas in Australia of wheat are fertilised with approximately 5 kg N ha^{-1} y^{-1} mono- or di-ammonium phosphate, these rates of N deposition are low compared with annual application rates of 50–80 kg N ha^{-1} for cereal crops. Nitrogen fertiliser application rates for high yielding crops such as vegetables and sugar cane are frequently of the order of 200 kg N ha^{-1}. Much of this N is volatilised and distributed by atmospheric transport both locally and continentally and in many cases the deposition arising from upwind fertiliser usage is an additional flux of N into an ecosystem with an existing N cycle close to equilibrium. This recycling of fixed N via atmospheric transport has not been studied or quantified in Australia. In Europe and North America, sustained atmospheric N deposition rates of 35 kg N ha^{-1} have been observed to stimulate the N_2O emission rate from forest soils six-fold through soil acidification (Brumme and Breese, 1992). Even greater responses were reported by Butterbach-Bahl et al. (1998) who found that inputs of NH_4^+ of 1 kg N ha^{-1} by wet deposition increased the N_2O flux by 2.4-fold and the NO flux by 9.5-fold in a temperate spruce forest in Germany.

Table 5. Nitrogen deposition in Australia

Location	**Dry deposition (kg N ha^{-1} y^{-1})**			**Wet deposition (kg N ha^{-1} y^{-1})**	
	NO_2	HNO_3	NH_3	NO_3^-	NH_4^+
Background marine					
Cape Grim	0.001	–	0.04	0.13	0.07
Natural					
Charles Point	0.28	0.55	–	–	
Darwin	–	–	–	0.94	0.25
Jabiru	–	–	–	0.67	–
Katherine	–	–	–	0.59	–
Agricultural rural					
Wagga	–	–	–	0.43	–
Coffs Harbour	–	–	–	0.91	–
Airsheds of coal-fired power stations					
Hunter Valley					
Murrurundi	0.76	0.73	–	0.71	–
Singleton	2.30	1.46	–	0.74	–
Muswellbrook	2.23	1.55	–	0.66	–
Latrobe Valley					
Warragul	1.4	–	–	0.66	–
Latrobe Valley Airport	1.4	–	–	0.71	–
Rosedale	1.4	–	–	0.59	–
Wilung	1.4	–	–	0.88	–
Urban airsheds					
Sydney	4.48	–	–	2.34	–
Lithgow: Site 1	3.25	3.99	–	1.02	–
Site 2	0.49	1.19	–	0.84	–
Site 3	0.69	0.90	–	0.99	–
Site 4	0.74	1.23	–	0.78	–
Port Phillip Bay[a]	0.9	0–2.5	0.002–0.02	2.5–4	3–6

[a] Estimated ranges determined by a literature review

In summary, the following are the important features of the atmospheric N deposition.

1. Nitrogen compounds are critical components of atmospheric chemistry and most species are ultimately converted to inorganic oxides or inorganic aerosol.
2. The atmosphere is an efficient medium for transport of N compounds both regionally and continentally. Based on overseas studies, large amounts of N are exported from the industrial cities to the regional and remote forests and grassland. Similarly when N fertiliser is added to an ecosystem, particularly in high concentration, it is often dispersed to nearby and remote regions first by transformation to gaseous species, then transport through the atmosphere and finally by deposition.
3. The form in which fixed N is deposited is not always the form in which it was emitted.
4. The environmental consequences in Australia of this atmosphere transport and re-deposition of N is unknown.

The road ahead

The issues

Four environmental problems have stimulated extensive research into N cycling through the atmosphere.

1. Soil acidification, which is a major issue in Europe and the USA. Both Europe and the USA have established comprehensive programs investigating acid deposition eg. the U.S. National Acid Precipitation Program (NAPAP, 1991).
2. Global warming for which N_2O is a direct greenhouse gas contributing approximately 4% of the increased radiative forcing in the atmosphere caused by anthropogenic emissions, and NO_x is a precursor of tropospheric ozone, which is also a potent greenhouse gas. The global budget of N_2O is still poorly understood, but it is well recognised that other N compounds can be readily transformed to N_2O through soil metabolism and therefore constitute indirect sources of N_2O. Nitrogen cycling in the biosphere is therefore an important scientific question for global warming issues.
3. The ultraviolet shield of the earth, maintained by ozone in the stratosphere and troposphere, is diminished by the release of N_2O but enhanced in the troposphere by the release of NO_x.
4. Nitrogen deposition over land and the oceans is stimulating productivity and enhancing the sequestration of atmospheric carbon dioxide.

To address these issues, inventories of anthropogenic and total emissions of N species, and measurements of N deposition are essential. Much of the work in Australia has been concerned with:

1. Determining emission factors and emission rates for industrial and biological emission sources.
2. Quantifying the climatology of atmospheric concentrations of N species in key regions.
3. Quantifying atmospheric N deposition particularly in airsheds affected by major industrial plants such as coal-fired power stations.
4. Quantifying and understanding the soil metabolic processes that control fixed N emission rates; and
5. The chemistry of polluted urban and clean remote tropical and marine atmospheres.

Big questions and research gaps

While industrial sources of N species are known with limited confidence, there are very few studies in Australia of NO_x and other N species emissions from natural or manipulated soils. These data are essential for quantifying emissions from the biosphere. Similarly, with respect to atmospheric loss processes, the current data set is extremely sparse. As techniques improve, more species are detected and the tendency has been for the more recent more comprehensive studies to return higher rates of N deposition. It is quite likely that the current estimates of N depositions when applied across the continent underestimate the actual rate of N deposition.

The big questions concerning the atmospheric N cycle over Australia are:

Table 6. Summary of typical N deposition in Australian environments

Location	Dry deposition (kg N ha^{-1} y^{-1})			Wet deposition (kg N ha^{-1} y^{-1})		Total N (kg N ha^{-1} y^{-1})
	NO_2	HNO_3	NH_3	NO_3^-	NH_4^+	
Oceanic	0.001	0	0.05	0.1	0.1	~0.3
Remote/Rural	0.3	0.6	–	0.8	0.3	~2
Airsheds of coal-fired power stations	2	1.5	0.1	0.6	0.2	~5
Urban airsheds	2	2	0.1	3	4	~11

1. Is atmospheric deposition a significant source of fixed N for any biological systems in Australia (dry and wet deposition)?
2. Can fixed N loss (dust rise, biological, chemical and pyro denitrification) to the atmosphere lead to depletion of fixed N in any Australian ecosystems (dust rise, biological, chemical and pyro denitrification)?
3. Is fixed N released from fossil fuel sources contributing significantly to the N balance of any ecosystems in Australia?
4. What role has fixed N loss (N_2O, NO, NH_3) from Australian terrestrial, freshwater and coastal ecosystems have on the functioning of the regional and global atmosphere?
5. Are there any unknown couplings between the atmospheric N cycle over Australia and the pathways to sustainable use of our natural resources?
6. Does transport of fixed N (and Fe) through the atmosphere from the Australian continent to the surrounding oceans contribute significantly to marine productivity and to the uptake of carbon dioxide by the surrounding oceans?

Examples of current work in Australia

Work currently in progress or planned in Australia indirectly addresses some of these issues, but in general the projects are directed at immediate environmental problems related to the N cycle, rather than comprehensively defining the N cycle in Australia. These projects include:

1. Studies of smoke emissions from biomass burning and the dispersion of smoke plumes in northern Australia that will help elucidate the N emissions from biomass burning.
2. Determination of emission factors for reactive and toxic trace gas species from domestic wood burning.
3. Emissions of N_2O and NO from agricultural and natural ecosystems.
4. The development of inventories and processed-based models of NH_3, NO, and N_2O emissions suitable for use in GIS systems and regional atmospheric chemical transport models.
5. Compilation of the national greenhouse gas emissions for non-CO_2 gases (including N_2O and NO_x from the biosphere and emissions of toxic gases from biomass burning.

The current research program is not addressing several key research gaps concerning the atmospheric N cycle and its ecological influences over Australia.

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Agricultural sources of nitrogen to aquatic systems

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Introduction

Agriculture is considered a major non-point source of increased stream loadings of nitrogen (N) in rural catchments in Australia. It is also implicated in the elevated nitrate levels found in groundwaters in some areas. While effects on water quality from agricultural point sources of N (eg. discharges of effluents to streams) are now generally well recognised, many issues concerning non-point sources of N remain unresolved.

The following are three key questions concerning N management in rural catchments in Australia:

- What is the extent of agricultural impacts on delivery of N to streams and groundwaters?
- What are the key processes of N transport and transformation from farm paddocks to streams and groundwaters?
- What are the major concerns and management options to reduce agricultural impacts on water quality?

We have a broad, general knowledge of these topics, but our lack of understanding of a number of key issues is a barrier to the development and adoption of more sustainable farming systems in Australia. Concepts of N dynamics and the identification of management priorities that have been developed from research in the northern hemisphere (mainly North America and the UK) in many cases may be inappropriate for Australian conditions, because of major differences in climate, soils and farming systems. Recent international reviews of agricultural non-point source pollution include those of Carpenter et al. (1998) in the US and Wilson et al. (1999) in the UK. Current Australian research is aimed at addressing the above three questions.

Defining agricultural impacts on water quality

In most Australian catchments, the effects of agricultural non-point sources on downstream water quality have at best been inferred qualitatively, but have not been well defined or quantified. This is largely because of the complexities of factors and interactions that occur at a large catchment scale, making it very difficult to associate cause and effect. This is particularly the case for N. The temporal and spatial variability in stream N concentrations that is inherent in natural, non-impacted systems (eg. due to N transformations, rainfall, temperature, etc.) is compounded by variability caused by agricultural management practices such as seasonal cropping patterns. Thus, it is often not possible to attribute with confidence the causes of elevated stream N levels from a simple analysis of monitoring data, particularly in large catchments.

The complexity of natural systems at a catchment scale almost inevitably requires a numerical modelling approach to be taken in order to evaluate specific land-use impacts. However, errors associated with catchment-scale water quality models can be very large, particularly for N (Moore and Gallant, 1991). Data requirements are often very extensive and even the more complex conceptual models are limited by our ability to fully understand and mathematically describe the processes that occur. Nevertheless, modelling can be a very powerful tool for analysing large data sets to draw out conclusions that would not be possible otherwise.

For example, research carried out in the Johnstone River catchment (1,634 km^2) in the wet tropics of north Queensland was able to clearly demonstrate the impacts of different land-use practices on stream loadings of N (Hunter and Walton 1997). A hydrological/water quality model (HSPF; Bicknell et al., 1993) was used, calibrated with data from six years of intensive monitoring and run with 39 years of rainfall records for the catchment. Modelled estimates showed that, on a unit area basis, long-term average N exports from cropping areas in the catchment (sugarcane and bananas) were approximately 40 kg^{-1} ha^{-1} y^{-1}, over four times that exported from rainforest areas (Figure 1). By comparison, N export from beef pastures was similar to that from rainforest, with dairy pastures exporting, on a unit area basis, approximately twice the N of rainforest and beef pastures.

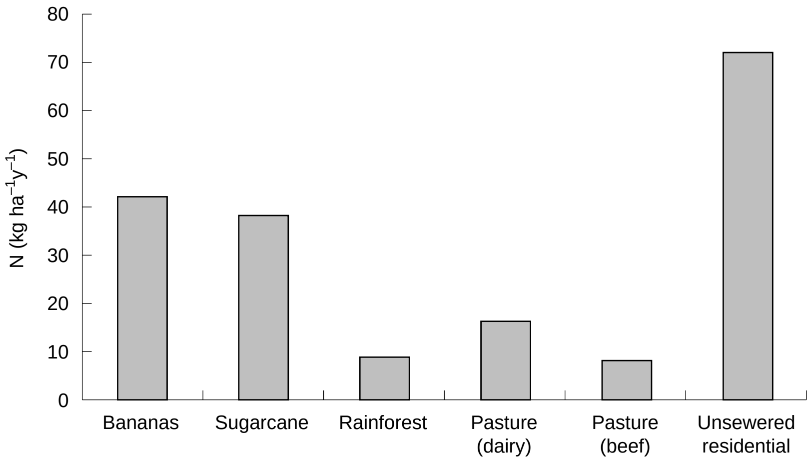

Figure 1. Modelled estimates of long-term average N export rates from different land uses in the lower Johnstone River catchment, based on 39 years rainfall records.

Overseas studies have reported a trend for increasing nitrate concentrations in catchment streams with increasing development (eg. Peierls et al., 1991; Keeney and DeLuca, 1993) and this has also been found in Australia. For example, in the Johnstone catchment, modelled estimates of catchment exports before land clearing (ie. assuming 100% rainforest cover), indicated that by far the greatest increase in nutrient exports has occurred in N (50% increase), especially nitrate (480%); by contrast, estimated increases in suspended sediment and phosphorus exports were around 25% (H. Hunter and R.S. Walton, unpublished data). Although underpinned by some significant assumptions, this was consistent with modelled estimates of present-day nitrate exports from the Johnstone, where, on average, 48% of total catchment exports of nitrate were found to come from areas growing sugarcane, which represented only 12% of the total land area of the catchment (Hunter and Walton 1997).

Few studies have the opportunity to amass the large data sets required to calibrate a complex model. As a consequence, simpler catchment models have been developed, particularly for use in land use planning and policy development (eg. CMSS, AQUALM, AGNPS and SWAT). These vary in their complexity and data requirements, but typically they rely on inputs of data on annual nutrient export rates (such as those in Figure 1). Unfortunately, such data are scarce and are generally relevant only to the conditions for which they were derived, so that large errors may occur in extrapolation to other catchments with differing soils, climate, management practices, etc. Caution should be exercised in using these models in such situations.

Simpler models have application for broad assessment purposes, but where reliable definition of land-use impacts on water quality in particular catchments is required, they need to be used with appropriate event-based water quality data that are specific to land uses in the catchment. Studies at a smaller scale potentially have somewhat fewer complexities, particularly in situations where there is a single or dominant land use, although such locations can be difficult to find at a scale of sufficient size to be relevant. Typically, several years of monitoring data are required to characterise water quality and nutrient loads over the range of flow conditions likely to be experienced in a catchment.

Nitrate contamination of groundwater is a major issue of concern in North America and Europe, where it has been associated with intensive animal production systems and overuse of N fertilisers and manures (eg. OECD, 1986; Skinner et al., 1997). Moreover, in some cases large reserves of nitrate have been found deep in soil profiles, representing additional nitrate loadings that can be expected to reach groundwaters after a lag period of up to decades. Elevated nitrate concentrations have been found in groundwaters in some parts of Australia, although generally not on the scale or magnitude reported for the northern hemisphere (eg. Keating et al., 1996). Nevertheless, they are of concern in some areas regarding the quality of water for human consumption. High nitrate concentrations in groundwaters are also of concern for protecting aquatic ecosystems where there is the potential for groundwaters to be discharged to streams or coastal waters. Protection of groundwater ecosystems is an emerging field of research about which little is known at present.

Nitrogen transport and transformation in agricultural systems

Nitrogen inputs

Fertiliser usage is a major issue concerning the off-farm movement of N. The use of N fertilisers is essential for maintaining the productivity of most Australian farming systems and is likely to remain so, at least for the foreseeable future. Available N levels in most Australian soils are insufficient to meet crop demand and (with notable exceptions) relatively few farming systems rely on leguminous crops and pastures to provide the N required to achieve optimum production levels, particularly in northern Australia.

The use of N fertilisers in Australia has more than doubled over the last 20 years (Figure 2), the major forms currently used being ammonium phosphates (47% of total usage), urea (43%) and ammonia (6%) (Fertiliser Industry Federation of Australia Inc., 1997). Nitrogen is used predominantly in cropping areas across Australia, although there is significant usage of N on non-leguminous pastures in some regions. Application rates across Australia vary widely, depending on factors such as crop or pasture species, climate, soil type and intensity of production systems. Little or no N is applied to considerable areas of broad-acre cropping and extensive grazing lands in lower rainfall parts of northern Australia (and as a consequence, soils in these areas are being depleted of N). In general, higher rates are applied in irrigation areas where crop yields are less limited by water availability and the probability of achieving high yields is much greater. For example, typical application rates for cotton are 60–70 kg ha^{-1} y^{-1} of N for dryland (rain-fed) crops and 150–160 kg ha^{-1} y^{-1} for crops under irrigation (G. McIntyre, pers. comm.).

There is also increasing interest in the re-use on land of effluents and sludges from sewage treatment plants and intensive animal industries. In some situations these offer alternative sources of N for plant production purposes, as well as providing a means of safe disposal of waste products. However, as with inorganic fertilisers, the inappropriate application of organic wastes and manures can lead to off-site water quality problems caused by N pollution. Decision-support tools are now available to assist in the design and management of land-based waste re-use systems that are sustainable, in terms of minimising the potential for excessive soil nutrient loadings and possible off-site transport (eg. Davis et al., 1995).

The recovery of fertiliser N in harvested product is often much less than 50% of that applied (eg. Moody et al., 1996; Myers, 1998). Some of the remaining N is retained in crop residues and the soil mineral and organic fractions; the remaining N is lost to the soil–plant system through processes of run-off, erosion, leaching, denitrification and volatilisation. Relatively small amounts of N (probably around 10 kg N ha^{-1} y^{-1} or less) are gained in precipitation, at least in rural Australia (eg. Wetselaar and Hutton, 1962; Steele and Vallis, 1988; Moody et al., 1996; H.M. Hunter and R.S. Walton, unpublished data).

The N loadings in intensive livestock industries such as cattle feedlots, dairies and piggeries tend to be high, since large numbers of animals are managed on relatively small areas of land. The situation is exacerbated where much of the N is imported as feed, rather than grown on site. Without careful management, there is thus the potential for significant off-site movement of N from land occupied by these industries.

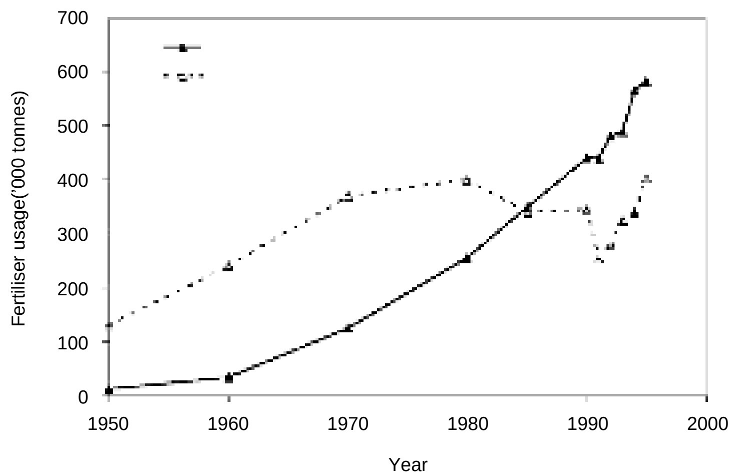

Figure 2. Fertiliser usage in Australia, 1950–1995 (from Fertiliser Industry Federation of Australia Inc. 1997).

Key processes of nitrogen transport

Apart from the removal of harvested product, the major pathways for N loss from crops and pastures are via processes of leaching, surface run-off, denitrification and volatilisation. Nitrogen is transported off-site in gaseous, dissolved or particulate forms.

The loss mechanisms and the extent to which they occur are dependent on many factors, including climatic conditions, soil type, amount of soil cover, type of cultivation and timing of rainfall relative to fertiliser or manure applications. This is a field of recent and current Australian research, with information on these processes becoming available, measured under defined sets of conditions at point-scale (ie. from small plots or paddocks), for a range of farming systems (eg. Moody et al., 1996). Complex numerical models (eg. CREAMS, GLEAMS) are available that can predict N losses at this scale and estimate the effects of different management practices (Gallant and Moore, 1991; Hook, 1997).

Particulate N losses are associated with wind and water erosion. The latter is generally the dominant process impacting on downstream water quality in most catchments. The particulate N fraction in run-off may include suspended organic matter (eg. from plant litter) and eroded soil particles. The finer soil particles are the most susceptible to erosion by run-off and once entrained are likely to travel furthest (Rose and Dalal, 1988). In some soils these fine particles are the most nutrient-enriched grain size fraction, thus exacerbating their likely impacts on aquatic ecosystems. Run-off typically also contains dissolved mineral and organic N, the concentrations and relative proportions being highly variable and depending on factors such as the timing and method of recent fertiliser applications and the age and amount of plant litter on the soil surface.

Several Australian studies have shown that, in terms of total loadings, most of the annual sediment and nutrient delivery to streams occurs during the relatively few brief periods of major run-off events (eg. Cullen et al., 1978; Cosser, 1989; Hunter et al., 1996). Moreover for N, elevated stream nitrate concentrations may be also a concern, and this may be related more to groundwater inflows than delivery in overland flow during events. As a consequence there may be a time lag before stream nitrate concentrations increase, and concentrations may then remain relatively high for longer periods than found for nutrients delivered by overland flow.

Nitrogen is leached through the soil profile predominantly as nitrate, generally with much lesser amounts of organic N and ammonium. Improved sub-surface drainage of agricultural lands, for example in irrigation areas, can increase off-site movement of nitrate (eg. Thomas et al., 1995).

In certain situations, losses of N through ammonia volatilisation from applied urea fertiliser can constitute a significant proportion of the amount applied (eg. Steele and Vallis, 1988). Considerable N loss can also occur through ammonia volatilisation from the urine and faeces of grazing animals and from ponded livestock effluent. At least some of the ammonia may subsequently end up in streams via rainfall and run-off, but the significance of this process in terms of water quality is not well defined. Denitrification losses from agricultural lands are probably of benefit to water quality, in helping reduce potential delivery of N to streams and groundwaters (although there may be concerns regarding global warming and ozone layer depletion in situations where nitrous oxide emissions are significant).

Larger scale processes

At present, one of our major limitations is our inability to 'scale up' from measurements and understanding of processes that occur at the point scale to those applying at larger hill-slope or catchment scales. Research currently proposed by the Cooperative Research Centre (CRC) for Catchment Hydrology will address some of these issues. While we have a broad appreciation of the N processes that may occur, we cannot at present quantify or model N fluxes via these various pathways, to take into account the complexity of interacting factors that can prevail at those scales.

Depending on the situation, significant pathways and processes influencing N transport on hill-slopes may include: soil erosion, sediment deposition and re-entrainment; shallow sub-surface flows of water and solutes; leaching to regional aquifers; and various N transformation processes (eg. denitrification, immobilisation, volatilisation, mineralisation and plant uptake). These processes can have a marked influence on N delivery to streams or groundwaters; for example, nitrate concentrations can be greatly reduced by denitrification and plant uptake in the riparian zone. Similarly, much of the soil eroded from land surfaces in catchments may be deposited down-slope and not delivered to catchment waterways. It is thus not possible to extrapolate with confidence from point-scale measurements of off-site losses to likely stream (or groundwater) loadings. There has been little research conducted in Australia on N processes at this scale.

Management options for more sustainable farming systems

It is now recognised nationally that a holistic, integrated approach is required for the sustainable management of natural resources in catchments, in keeping with the principles of ecologically sustainable development. These principles underpin the National Water Quality

Management Strategy's guidelines for water quality management in rural catchments, including the development of strategies for reducing non-point source pollution (ARMCANZ and ANZECC, 1996). The involvement of stakeholders in decision-making processes and the development and adoption by industry of best management practice guidelines are key elements of these strategies.

There has been significant progress in recent years towards developing more sustainable farming systems, at least in some rural industries. Notable examples include the adoption since the 1980s of erosion control measures such as contour banks, minimum tillage and the retention of crop residues to protect the soil surface. However, in other regards progress has been slow, and the need to consider environmental as well as productivity-related issues has not always been readily accepted by primary producers. To some extent this has probably been exacerbated by our inability as scientists to understand and communicate the issues and offer management alternatives that are practical and economically viable.

For many farming systems, the economic costs of off-site losses of N are relatively minor compared with the overall costs of the farming enterprise, so there may be little incentive for farmers to reduce N losses, from a purely economic point of view. This represents a major challenge in terms of gaining widespread adoption of more ecologically sustainable farming systems.

In general terms, on-farm management practices with the potential to assist in minimising off-site movement of N include the following:

- more efficient and ecologically sensitive use of N fertilisers, through;
  - use of split applications;
  - use of slow release fertilisers;
  - provision of better information on crop requirements;
  - applying fertilisers below the soil surface;
  - adoption of more accurate methods for identifying fertiliser needs (better soil tests) combined with more accurate application techniques (eg. use of GPS systems on tractors);
  - use of nitrification inhibitors;
- use of leguminous crops and pasture species, including breeding high yielding varieties that are more efficient N fixers (and in the long term, genetically modifying non-leguminous crop species, eg. wheat, to fix N);
- retaining crop residues to i) immobilise N; and ii) maintain cover on the soil surface;
- adoption of zero till or minimum till practices to help minimise erosion losses of N (although in some situations this may increase the risk of nitrate leaching to groundwater);
- minimising bare fallow periods;
- use of deep-rooted crops and pastures to retrieve N from depth in the soil profile;
- use of vegetative buffers along farm drainage lines to trap sediment and associated N;
- ponding of irrigation tail water and run-off to reduce nitrate concentrations through denitrification;
- restricting stock access to streams; and
- use of constructed wetlands to reduce N concentrations.

Several of these topics have been the focus of recent or current research, although much more is required on many issues before adequate information is available to cover the diversity of farming systems and environments that typify Australian agriculture. However, even with the adoption of best management practices to minimise off-farm transport of N, it is almost inevitable that some inefficiency of N use will occur and lead to leakage of nitrate. Nitrate is highly mobility and rainfall is unpredictable, particularly in northern Australia.

Once mobilised, the best opportunities for arresting nitrate delivery to streams lie in having appropriate riparian buffer zones and wetlands in place to foster denitrification and plant uptake. Defining the effectiveness of riparian zones in reducing nitrate loads has been a priority research topic in north America and Europe over the last 10–20 years (eg. see reviews by Correll (1997) and Gilliam et al. (1997)) but to date little research has been carried out in Australia.

As noted previously, conclusions drawn from overseas experience may not be relevant in Australia because of the vastly different climate, geology, soils and flow regimes. A multi-disciplinary research program on N and carbon (C) dynamics in riparian zones and wetlands is currently being developed by the CRCs for Catchment Hydrology, Freshwater Ecology, and Coastal Zone, Estuary and Waterway Management. Major objectives are to identify key factors influencing N and C transport and transformations in riparian buffer zones and to determine optimum riparian zone characteristics for effective reduction of nitrate loads delivered to streams.

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Nitrogen sources — sewage and stormwater

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Introduction

Point source sewage discharges have long been known as major nutrient inputs to receiving waters and as having a detrimental impact on aquatic ecosystems (Hynes, 1960). While point source discharges have a variety of impacts, nutrient (nitrogen) enrichment is an important factor in the eutrophication of receiving waters. However, as wastewater point source discharges have been progressively improved or removed through more widespread sewering, the impact of stormwater has become a more obvious problem.

2. Sewage and urban stormwater quality

The quality of both sewage discharges and stormwater run-off can have considerable spatial and temporal variability. Table 1 provides some examples of nitrogen (N) water quality for natural waters, sewage, urban run-off, and urban stream flow.

As can be seen from Table 1, the concentration of certain N species (eg. ammonium) can be several orders of magnitude greater than background concentrations. At these concentrations ammonium is not only a nutrient but also a toxicant. Point source sewage discharges typically have a major impact on the water quality and ecology of receiving waters. Figure 1 illustrates the effect sewage effluent discharge can have on stream water quality. A similar response can be seen over a longer time period at the catchment scale. Figure 2 shows a gradual improvement in water quality over a 10-year period (1978–1988) as a result of the removal of point source discharges and development of the sewerage system. While both Figure 1 and 2 show dramatic improvements in water quality after the removal of major sewage inputs, the post-sewage input water quality is still very poor and reflects the more diffuse impacts of urban run-off. Regular and pronounced seasonal variation in water quality is also evident after the removal of the sewage inputs. Dandenong Creek has a large catchment and while significant urbanisation has resulted in major modifications to its channel in a number of reaches it also has large reaches of relatively 'natural' channel. It appears that significant biological processing (aquatic plant uptake, denitrification) of nitrate is occurring.

In the urban environment, sewage and surface run-off are never really separated as sources of nutrients to receiving waters. In most of Australia, sewerage and drainage are separated systems. Sewerage systems are normally designed to completely contain sewage flows from a catchment. However, no piped system is ever watertight. Consequently, during periods of wet weather, water can infiltrate the sewer and exceed the flow capacity of the system. To prevent backup of the sewer, emergency relief structures are built into the sewer to allow the system to overflow. In general, the older the infrastructure and the more developed the catchment is, the greater the frequency of sewer overflow. The older the sewer the more leaky it tends to be. Similarly, the older and more developed the catchment the greater the number of illegal stormwater connections to sewer. These factors result in an increased frequency of sewer overflow in wet weather.

In older urban catchments, the reverse can also to occur and there can be a greater number of illegal connections of sewer to stormwater. This results in poor dry weather quality in the drainage system. This situation probably explains the high ammonium results in the dry weather data of Rowlands et al. (1992) from Sydney shown in Table 1. Figures 3 and 4 illustrate a similar pattern. Figure 3 shows a period of recent stream flow water quality for Dandenong Creek. Most of Dandenong Creek catchment has a relatively modern sewerage and drainage infrastructure. While the absolute concentrations are high compared with natural waters, the variation, which is related to flow, is relatively low. The presence of significant ammonium concentrations can be considered as indicative of sewage input. The ammonium concentrations in Dandenong Creek at Stud Road are low and few spikes are evident. This suggests little overflow of sewage into the system. The concentrations are probably largely indicative of surface run-off in an urban catchment.

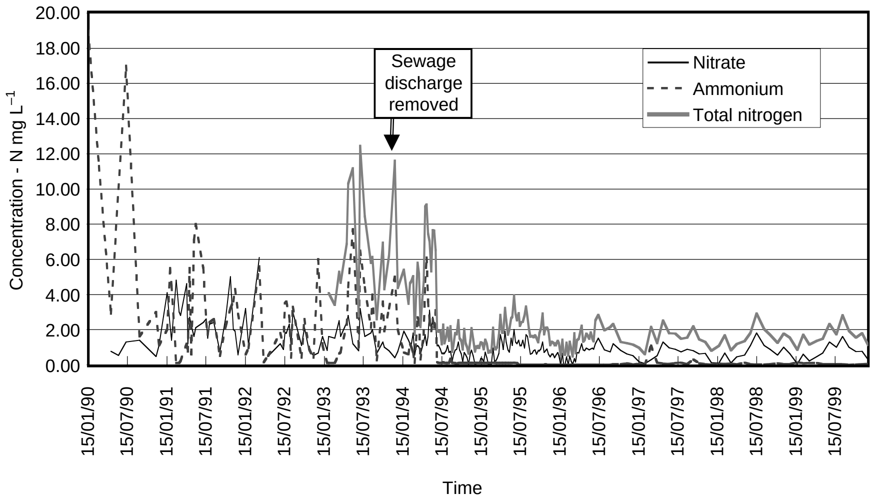

Figure 1. Dandenong Creek water quality at Pillars Crossing showing the impact of a point source sewage discharge

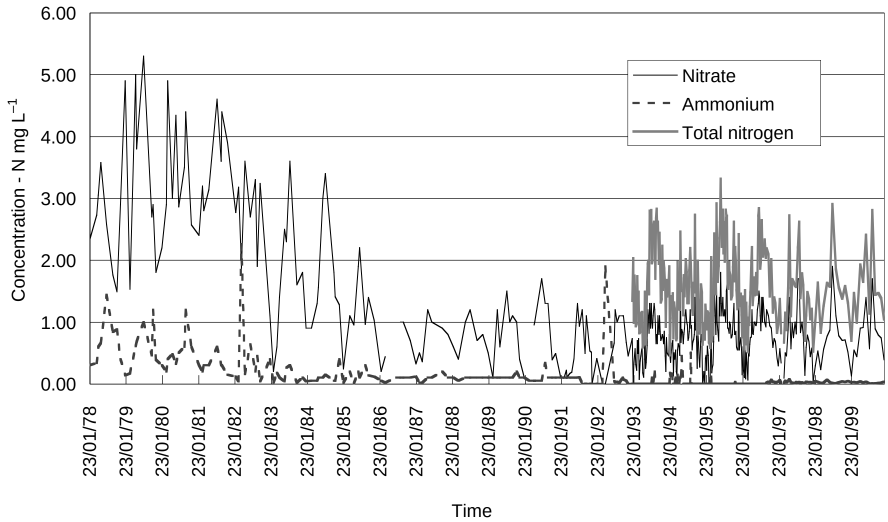

Figure 2. Dandenong Creek at Stud Road showing the gradual improvement in water quality as a result of the removal of point source discharges and improved sewerage

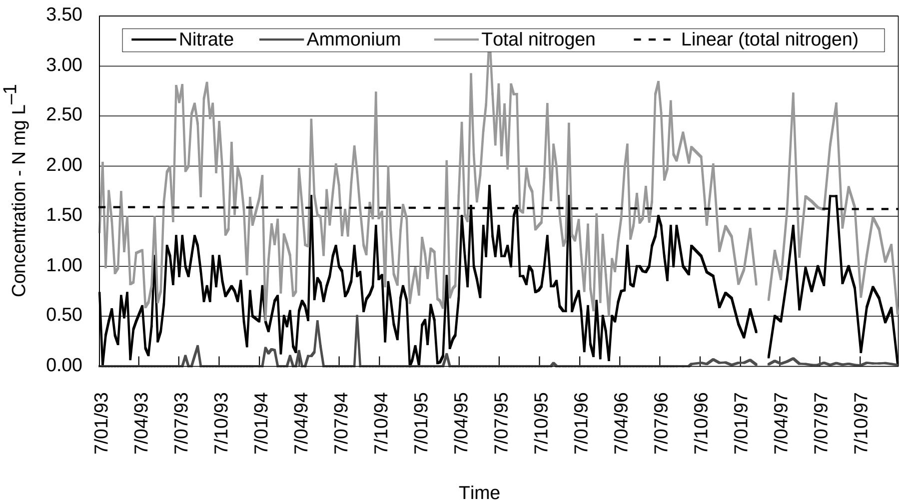

Figure 3. Dandenong Creek stream flow nitrogen water quality at Stud Road, Roveville

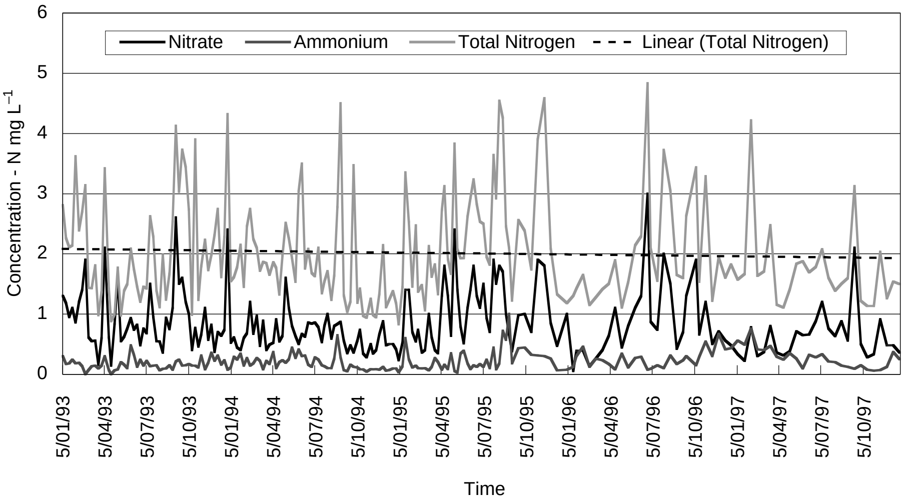

Figure 4. Gardiners Creek stream flow nitrogen water quality at Glenferrie Road, Hawthorn

Table 1. Indicative water quality for natural waters, sewage, run-off and urban stream flow

Reference	Water type	Data type	Ammonium	Oxidised nitrogen	Total nitrogen
			Concentration (mg/L)		
ANZECC (1992)	Natural waters	Typical background levels	0.02–0.03	–	0.1–0.75
O'Loughlin et al. (1992)	Sewage	Typical secondary treated	20	10	35
O'Loughlin et al. (1992)	Urban stormwater	Literature values (mean & range)	0.7 (0.1–2.5)	1.5 (0.4–5)	3.5 (2–6)
Mudgway et al. (1997)	World stormwater	Literature values (mean)	–	–	2.5
	Australian stormwater	Literature values (mean)	–	–	2.6
Williamson (1993)	World stormwater	Literature values (median & 10%–90% %tile)	0.10 (0.03–0.25)	0.80 (0.38–1.5)	2.5 (1.3–4.3)
Rowlands et al. (1992)	Bondi wet weather	Urban run-off (median & range)	– (0.01–1.9)	– (0.01–3.4)	– (0.54–9.0)
	Bondi dry weather		0.06 (0.01–1.4)	3.5 (1.1–6.4)	4.4 (1.4–11)
	Greendale wet weather		– (0.01–0.6)	– (0.01–1.9)	– (0.39–4.2)
	Greendale dry weather		0.06 (0.01–5.6)	1.4 (0.01–2.7)	2.2 (0.71–9.1)
Melbourne Water Corporation, Water Quality Database (1992–1999)	Koonung Creek	Stream flow (median & range)	0.05 (0.003–0.53)	0.54 (0.04–3.7)	1.5 (0.64–5.8)
	Gardiners Creek		0.16 (0.02–1.0)	0.70 (0.05–3.0)	1.8 (0.83–4.8)
	Dandenong Creek		0.03 (0.01–0.05)	0.75 (0.01–1.9)	1.5 (0.46–3.3)

Figure 4 shows a period of recent stream flow water quality for Gardiners Creek. Gardiners Creek is a fully developed urban catchment with a relatively large proportion of old sewerage and drainage infrastructure. Nitrogen concentrations are higher and much more variable than in Dandenong Creek. In particular, there is a continuous ammonium signature. This would suggest sewage is almost a constant nutrient source in this catchment regardless of flow conditions. The very strong seasonal pattern in the Dandenong Creek data is not evident in the Gardiners Creek data. The channel of Gardiners Creek has been very significantly modified over most of its length. Instream aquatic macrophyte communities are virtually absent from Gardiners Creek. It appears the capacity for biological processing in Gardiners Creek has been impaired.

Current and recent research

Sewage

The focus of much recent Australian research on sewage as a nutrient source has been of discharges to coastal environments. Major examples are Port Phillip Bay Environmental Study (CSIRO, 1996), Moreton Bay Study (Dennison & Abal, 1999), Effluent Management Study Eastern Treatment Plant (Newell et al., 1999). These studies all focus on the impact of various discharges on the receiving waters. The research aspect of these studies has largely focused on modelling ecological responses or impacts. The source data for many of these studies are from various analytical techniques, routine monitoring programs, and are typically poorly synchronised to flow conditions. Little or no work has focused on the N composition of wastewaters in recent times. Herrman et al. (1999) have investigated the role of urea in fish kills after overflows from combined sewers. There has been some recent work on phosphorus analysis (Halliwell et al., 1996) and sewage composition management (Cullen et al., 1995). The general theme of current research is towards modelling sewage impact on receiving waters. Little attention is being paid to improving the quantification and characterisation of sewage discharges. The argument against allocating resources to sewage characterisation is that the concentrations are generally so high compared with background concentrations that the form hardly matters. In general, the Australian approach to the management of point discharges of sewage has been to remove discharges to freshwater and direct them to land or coastal systems. Where this has occurred in a systematic way, impacts on the marine coastal waters can be expected if only through the input of freshwater (Newell et al., 1999). However, at least at the current levels of inputs, Port Phillip Bay has adapted well to sewage and stormwater inputs and shows little direct impact of nutrient enrichment (CSIRO, 1996).

Most overseas research focuses on combined sewer overflows (CSO) (Joliffe & Ball, 1999) which is not a common sewerage/drainage format in Australia. A recent review of overseas work in this area suggests either toxicants or simple organic pollutants are the focus of most of this work (O'Connor et al., 1999).

Stormwater

Most Australian States are concerned about the impact of urban stormwater on the ecology of receiving waters and have introduced management strategies or best management practice guidelines (Brisbane City Council, 1999; NSW Environmental Protection Authority, 1996; Victorian Stormwater Committee, 1999. However, as with sewage discharges, most research attention is focused on predicting and modelling stormwater flows and distantly followed by how to treat or improve stormwater quality. Little current research is focused on the nature of what has to be treated (Joliffe & Ball, 1999). Williamson (1993) and Duncan (1995a,b) have tried to address this problem by consolidating the available published information in literature/data reviews. Williamson (1993) provides a useful statistical summary of urban water quality, Duncan (1995a) provides an extensive database of urban stormwater quality references, while Duncan (1995b) provides a review of stormwater monitoring practice over the past 30 years.

The main source of N in stormwater include (see also Figure 5):

- atmospheric deposition (natural and industrial regional emissions);
- wash-off from natural catchment surfaces (leaching of natural materials and fertiliser);
- wash-off from impervious catchment surfaces (roofs (dry deposition, animal faeces—birds, possums etc.), roads and pavements (dry deposition, local vehicle emissions);
- wash-off of organic litter (natural riparian leaf fall. street tree leaf fall, grass cutting wash-off from waterway maintenance); and
- contamination from the sewerage system (overflows during wet weather, illegal connections during dry weather).

The quantification of these sources is poor. Furthermore, it is unlikely that these source have the same prominence in different locations. For example, the review by Duncan (1995c) of the international literature suggests that the atmosphere provides as much stormwater N as does wash-off from the catchment. The Sydney Coastal Stormwater Study (Rowlands et al., 1992), on the other hand, suggests sewer overflow and illegal cross-connections were a major source of N pollution (see high ammonium concentrations in Table 1 for both wet and dry weather flows in Bondi and Greendale drains).

There are clearly significant differences between the dominant sources of pollution in different catchments. However, as a point of discussion, and in the absence of data, I propose the following order for the likely N sources for a typical Melbourne urban catchment:

1. Wash-off of catchment derived material from impervious catchment surfaces (roofs (dry deposition, animal faeces—birds, possums, etc.), roads and pavements (dry deposition, local vehicle emissions).
2. Contamination from the sewerage system (overflows during wet weather, illegal connections during dry weather).
3. Wash-off from natural pervious catchment surfaces (soil erosion, leaching of natural materials and fertiliser).
4. Wash-off of atmospheric derived material from impervious catchment surfaces.
5. Wash-off of organic litter (natural riparian leaf fall, street tree leaf fall, grass cutting wash-off from waterway maintenance).

The order of importance for contaminant sources to stormwater is highly dependent on the land use, the extent and design of the road network, and the design and condition of the sewerage and drainage systems.

Gaps in research

Gaps in research or information regarding sewage and stormwater as sources to the environment primarily revolve around the mass of pollutant delivered to the environment and the pattern of delivery. These are crucial management questions. For example, in some ways a continuous, low-flow illegal connection of sewer to stormwater is easier to manage than the stochastic wash-off of organic litter into stormwater. However, at present we don't have the information to prioritise the importance of these as sources. For example, the discrepancies identified in the Moreton Bay study between modelled and measured values largely reflect our poor understanding in the detailed relationship between flow and concentration. Our conceptual understanding of it is reasonably good, but our quantitative understanding under a range of catchment and climatic conditions is poor.

In general, the determination of catchment run-off rates under various catchment conditions is an ongoing desire, but in practice this is difficult and costly work.

The following is a list of possible research and related activities on the role of sewage and stormwater as N sources.

- An improved understanding of the nature and availability of the organic fraction of total N. Apart from ammonium, what is total Kjeldahl nitrogen?
- An improved understanding of the balance between regional and local atmospheric sources of N. What is the relationship between regional industrial emissions versus local transport related emissions?
- Stormwater and sewage N inputs to receiving water are highly stochastic in the urban environment. We need to understand this relationship in order to clearly identify short and long-term impacts.

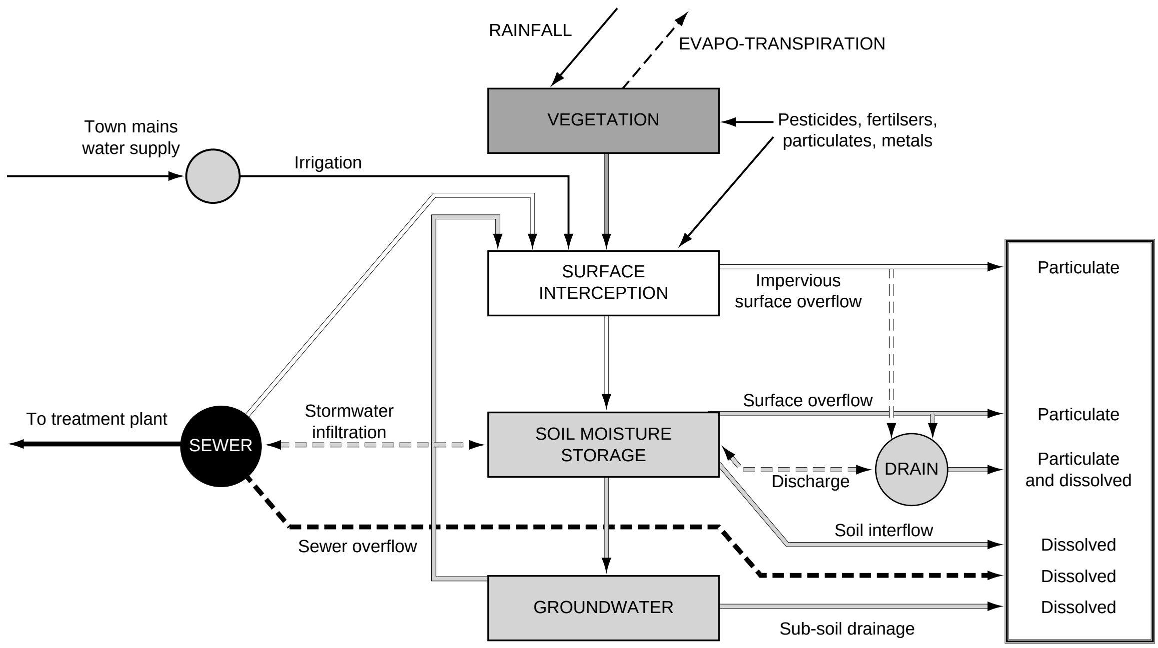

Figure 5. The major sources and pathways of urban pollutants (Ian Lawrence, pers.comm.)

- Owing to the stochastic nature of stormwater, event-based sampling is required to adequately described the pollutant flow relationship.
- Because of the performance variation in most wastewater treatment plants, significantly increased sample frequency is required to adequately describe the loads from most treatment plants.
- Any consideration of sources also needs to evaluate the receiving waters storage capacity and determine regeneration potential. Many receiving waters may not respond to contemporary loads but have a delayed response. The delay function may be determined by a complex set of conditions unrelated to the input load (eg. low flow, stratification etc.).

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Different methods for measuring rates of nitrogen transformation: strengths and weaknesses

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This paper will discuss the strengths and weaknesses of the various methods that are available to measure rates of nitrogen (N_2) fixation, nitrification and denitrification in aquatic systems. It focuses on methods that are currently being used in Australia (by researchers at this workshop) as well as covering other methods that may be worth considering in future work or that are currently being developed. Data from recent work is also presented with the appropriate method when it is available.

All techniques used to measure rates of nitrogen (N) transformation require that sediment or water samples be incubated in a closed system of some sort. Changes in the concentration of different N species are then measured over time to determine the rate of transformation. These techniques can be separated into five categories:

1. Those that assay for enzyme activity in samples by providing a substitute compound or blocking a pathway in the N cycle (Fig. 1), so that the accumulation of a compound that is not normally produced can be used to measure enzyme activity. Acetylene is the compound used most commonly for this purpose to measure rates of both N_2 fixation and denitrification.

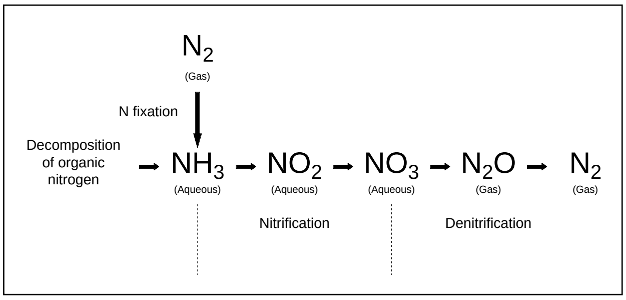

Figure 1. The nitrogen cycle; showing nitrogen fixation, nitrification and denitrification

2. Use of ^{15}N labeled N_2, NH_4 or NO_3 to track the transformation of N from one species to the next. This method has many advantages because of its ability to measure the absolute rates with minimal modification to the natural system. However, it still makes assumptions regarding the homogeneous mixing of the ^{15}N to the site of transformation (usually in the sediment).
3. Direct measurement of the product (N_2 gas for denitrification) under close to natural conditions. These methods while sounding preferable because they allow 'close to natural conditions' to be maintained, have the logistical problem that the atmosphere consists of approx. 80% N_2 (gas), thus providing a very large baseline to measure changes against.
4. Measuring all the products of decomposition (CO_2, PO_4, NH_4 NO_x) and using mass balance to infer if N is being lost due to nitrification followed by denitrification. This method relies heavily on knowing the C:N:P ratio of the organic matter that is being decomposed as this directly affects the results.
5. Stable isotopes ($^{14}N/^{15}N$) at natural abundance also provide a way to track the flow of N through an ecosystem as well as qualitatively identify regions were high rates of N cycling may be taking place. This method does not allow for quantitative measurement of transformation rates, but it does provide a cheap way to identify areas of a river system where transformation of N may be important.

The acetylene reduction and block techniques

Acetylene gas can be used to measure rates of both N_2 fixation and denitrification. The measurement of N_2 fixation is possible as the enzyme (nitrogenase) reduces acetylene (C_2H_2) to ethylene (C_2H_4) in preference to its natural substrate N_2 (Capone, 1988) (Fig. 2). The rate of denitrification can also be measured using acetylene gas as it blocks the last step of denitrification (conversion of N_2O to N_2) this allowing for the relatively easy measurement of N_2O using a gas chromatograph (GC). One disadvantage of this method is that it also blocks nitrification (the production of nitrate from ammonium), meaning that an external source of nitrate must be provided in samples with low ambient concentrations of nitrate. For this reason results from this method are often referred to as 'potential denitrification rates' as any substrate limitation that may occur in the natural system has been removed. However, if used within its limitations this method is an accurate, easy to apply, assay for enzyme activity. Seitzinger et al. (1993) found that the acetylene block was only 50% efficient and resulted in similar amounts of N_2O and N_2 gas being produced. As a result of this incomplete block the acetylene block method in a comparison between three methods was approx. 50% of the value obtained by the direct measurement of N_2. However, in the same experiment the acetylene block method measured rates 30% greater than the values obtained by the ^{15}N tracer experiment, probably because of poor mixing of the $^{15}N–NO_3$ from the water column into the sediment.

The acetylene block technique has been used at both Griffith University and Monash University for projects in the North Johnston and Brisbane rivers, Queensland, the Goulburn River, New South Wales and the Yarra River, Victoria (Figure 3). Bourgues (pers. comm.) has also performed experiments to look at variation in the method when different concentrations of nitrate or a carbon source are added (Figure 4).

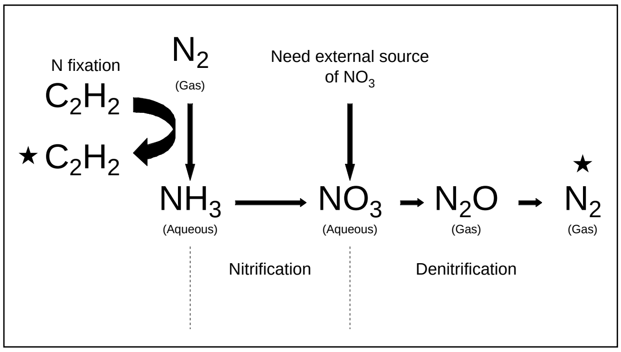

Figure 2. Acetylene gas affects the N cycle in several ways.

1) It is preferentially reduced by the nitrogenase enzyme to ethylene (H), so increases in C_2H_4 can be used to measure rates of N_2 fixation.

2) It blocks nitrification and the final step of denitrification so that increases in N_2O(H) can be used to measure rates if denitrification, provided an external source of NO_3 is provided.

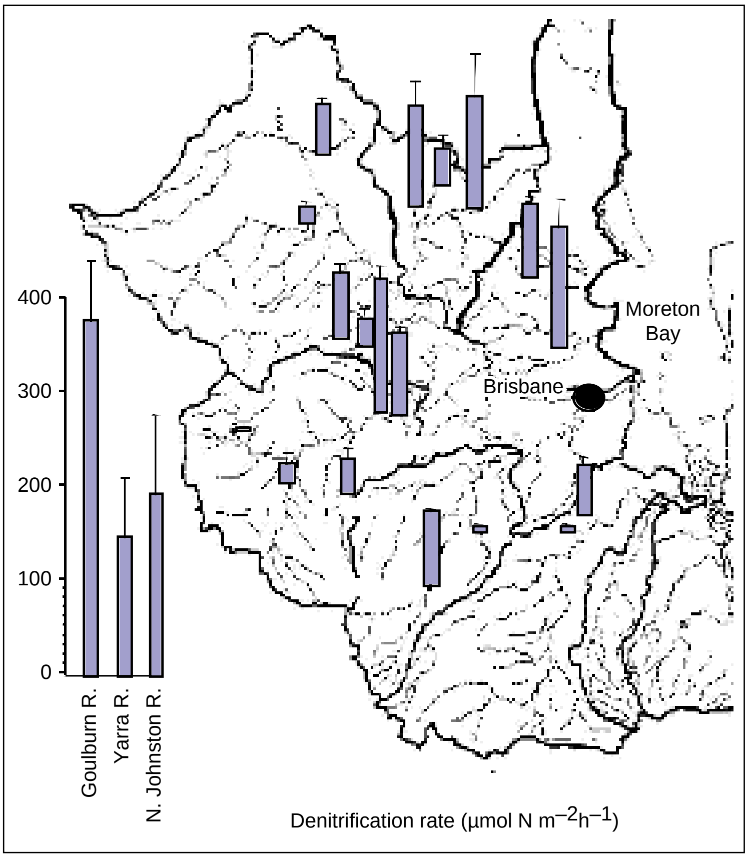

Figure 3. Denitrification rates measured using the acetylene block technique in February 2000 at 19 sites (mean ± SE, n=3) in the Brisbane Catchment, as well as comparable rates (mean ± SE, n=6–15) from the North Johnston, Goulburn and Yarra rivers (data from Goulburn and Yarra rivers provided by Sophie Bourgues, Monash University).

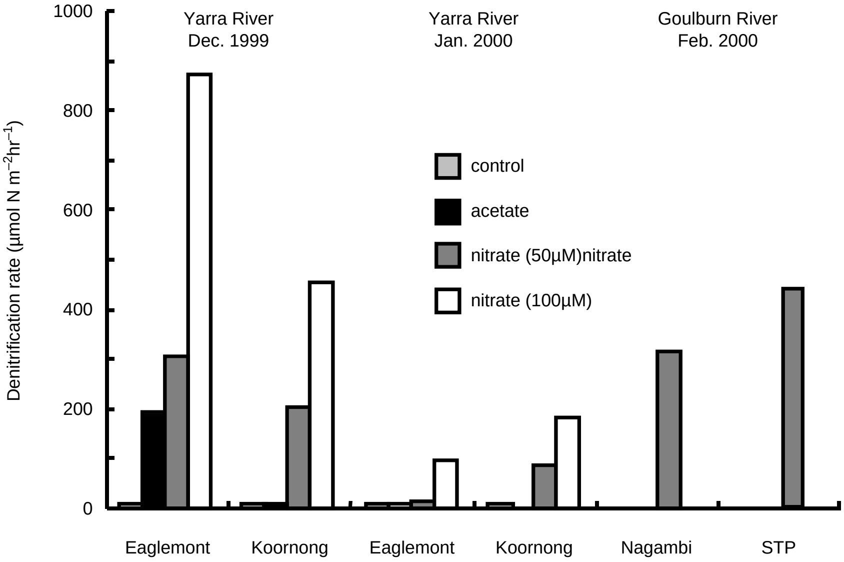

Figure 4. Denitrification rates measured using the acetylene block technique (mean, n=3) for two sites in the Yarra River (measured at two different times) and two sites in the Goulburn River. Four treatments were used: control; acetate added; 50 µM nitrate added; and 100µM nitrate added. (Data provided by Sophie Bourgues, Monash University.

^{15}N Tracer experiments

The use of ^{15}N-labelled N compounds allows for any step of the nitrogen cycle to be investigated, with the ability to measure both the rate of decline in the concentration of ^{15}N in the substrate and the appearance of ^{15}N in the product of any step (or several steps in the N cycle; Figure 5). The difficulties with this method are: 1. the same concentration of ^{15}N labelled compound may not be available at the reaction site (usually in the sediment) as is present in the overlying water (Seitzinger et al., 1993); 2. the addition of ^{15}N compound may stimulate N processing as it increases availability of N; and 3. this method is labour intensive in the analysis of samples.

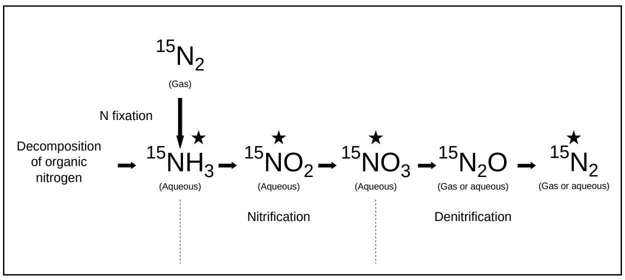

Figure 5. Labeled ^{15}N tracer experiments allow for the measurement of individual or multiple steps in the N cycle depending on which N compounds are added and which are measured.
★ Represents the most common compounds measured.

Direct measurement of N_2 production

The direct measurement of N_2 production (Figure 6) has advantages over both the acetylene block and ^{15}N tracer methods as it does not rely on diffusion of either introduced additional compounds that can have additional effects on microbial communities or substances to the reaction site. However, because of the large concentration of N_2 in the atmosphere, measuring small changes in N_2 is difficult. This problem is addressed by the introduction of a new technique (MIMS, membrane inlet mass spectrometry) to accurately measure small changes in N_2 under ambient conditions (Kana et al., 1998). At the moment there is a MIMS at the Australian Geological Survey Organisation (Canberra), Southern Cross University (Lismore, NSW) and Monash University (Melbourne), with the latter two installations in the final stages of being tested.

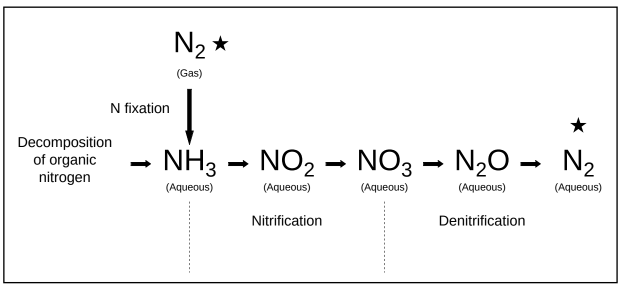

Figure 6. The direct measurement of changes in N_2 (★) can be used to measure the net effect of N_2 fixation and denitrification.

Using stoichiometry and mass balance

A less direct measure of denitrification in surface sediment can be obtained by using benthic chambers and measuring the fluxes of CO_2, NH_4, NO_x, and PO_4. The production of CO_2 (in the dark) is then assumed to represent the rate of decomposition of organic matter in the sediment. Using an assumed C:N:P ratio of organic matter available for decomposition, the rate of denitrification in the sediment can then be estimated as the difference between the observed DIN flux and that predicted based on stoichiometry (Figure 7). In a Moreton Bay study, both the acetylene block method and this method were used. However, with the exception of one site there was poor agreement between the results (Figure 8).

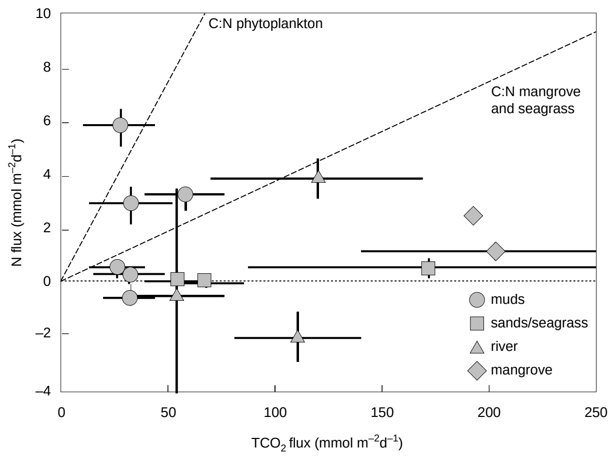

Figure 7. Example of how the stoichiometry method calculates denitrification rates. The denitrification method is calculated as the distance a point must move vertically (along the y-axis) to intercept the C:N ratio of its original carbon source. If there was no denitrification all points would be expected to fall on the C:N ratio line for either phytoplankton or mangrove/seagrass, depending on the carbon source (from Heggie et al. (1998) and Dennison and Abal (1999)).

Use of stable isotopes

The $\delta^{15}N$ values of organisms have been used to identify the principal sources of N in aquatic environments (Udy and Dennison, 1997b; 1998; McCelland et al., 1997), the trophic level of consumers (Peterson and Fry, 1987; Fry, 1991) or to identify sites were extensive N cycling or transformations are occurring (Owens, 1985; Fourqurean et al., 1997: Erskine et al., 1998). The use of $\delta^{15}N$ as a tracer of anthropogenic pollution is based on the assumption that there is minimal fractionation occurring between different stages in the nitrogen cycle, and that the $\delta^{15}N$ value of the plants reflect that of their N source (McClelland and Valiela, 1998; Dennison and Abal, 1999). This is likely to occur when nitrogen is the limiting nutrient in an ecosystem, as is the case in many marine ecosystems, and allows for the relative proportion of N contributed from sources with different $\delta^{15}N$ values to be calculated using mixing models.

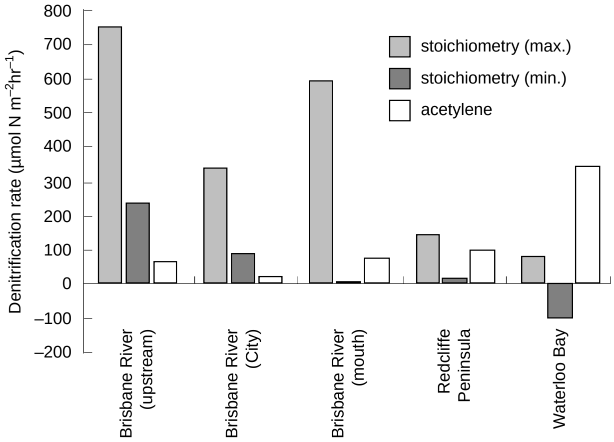

Figure 8. Comparison of the denitrification rates calculated by stoichiometry (mass balance) and acetylene block techniques at five sites in Moreton Bay (data from Heggie et al. (1998) and Dennison and Abal (1999))

When nitrogen is in excess, or when transformations occur to only part of the available N, it is possible to get large changes in the $\delta^{15}N$ values of plants due to fractionation between the ^{14}N and ^{15}N isotopes. Fractionation can occur during chemical and microbial transformations of N or during plant assimilation (Peterson and Fry, 1987; Erskine et al., 1998; Udy and Dennison, 1997a). This occurs as a result of chemical and biochemical transformations of N preferentially using the lighter ^{14}N isotope, resulting in enrichment of the ^{15}N isotope in the molecule or compound with the greatest bond strength (Peterson and Fry 1987). For example, decomposition of organic matter in estuaries can elevate the $\delta^{15}N$ value of suspended organic matter by about 8‰ (Owens 1985) and denitrification in seagrass sediment can result in about 5‰ enrichment in $\delta^{15}N$ values of the seagrass (Fourqurean et al. 1997).

In the North Johnston River, Queensland, $\delta^{15}N$ values of crops, riparian trees, as well as emergent and submerged aquatic vegetation were sampled from streams with disturbed (agricultural) and undisturbed (rainforest) catchments. Riparian and aquatic plants had similar $\delta^{15}N$ values in undisturbed streams, indicating a similar source of inorganic nitrogen. In disturbed catchments, however, aquatic plants had significantly higher $\delta^{15}N$ values than did the adjacent riparian vegetation, with highly disturbed catchments having $\delta^{15}N$ values 4–8 ‰ higher than adjacent riparian vegetation and aquatic plants from streams within undisturbed catchments. These elevated

$\delta^{15}N$ values of aquatic vegetation in streams with disturbed catchments are probably caused by high rates of microbial decomposition followed by incomplete denitrification in the stream bed (Figure 9).

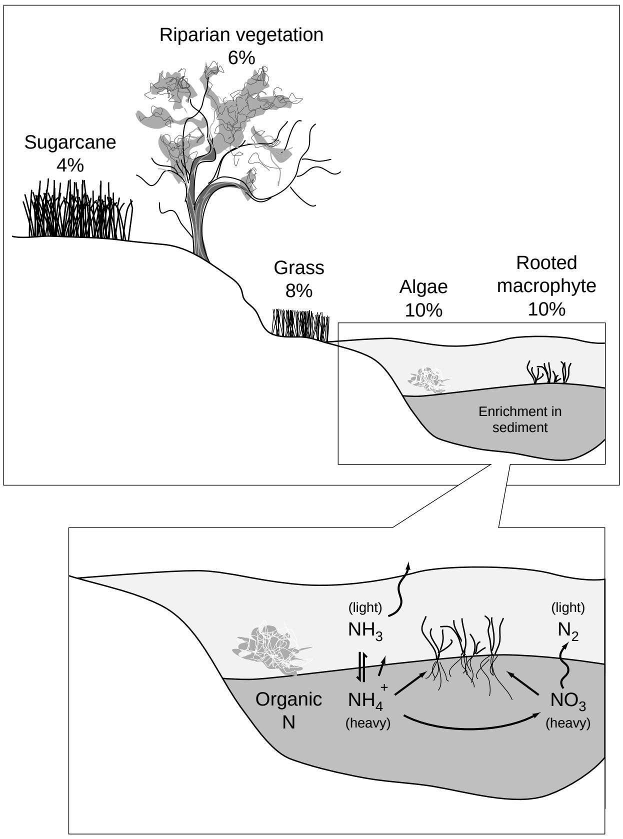

Figure 9. A) Variation in $\delta^{15}N$ values of vegetation at Bamboo Creek (a high disturbance site), moving from the agricultural crop (sugarcane) towards the stream. B) Proposed model for nitrogen cycling at disturbed sites; demonstrating two processes that would lead to elevated $\delta^{15}N$ values in N used by aquatic plants: (1) the thermodynamic equilibria between NH_3 and NH_4 and (2) denitrification.

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Nitrogen transformations in freshwater sediments

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Introduction

There is increasing recognition that inorganic nitrogen (N) species (ammonia, nitrate and nitrite), rather than phosphate, can be the limiting nutrients in freshwater systems. The N supply may not only limit the algal biomass, but affect algal succession also. In some cases, a low N:P is associated with the dominance of cyanobacteria, with negative impacts on water quality. Differences in the speciation of the available N (ie. ammonia versus nitrate) may alter the relative abundance of N-fixing and non N-fixing cyanobacteria (Blomquist et al., 1994).

Rivers deliver N species to estuaries and the sea where N is frequently the limiting nutrient. Anthropogenic inputs are increasing and there is considerable concern to establish what the sustainable load of N is before the estuary undergoes irreversible ecological change. This is already happening in some coastal waters. Large areas (~0–10^4 km^2) near the Mississippi mouth undergo prolonged hypoxia every summer because of the enhanced pelagic phytoplankton production supported by extra N from terrestrial agriculture (Turner and Rabalais, 1994).

Sediment N transformations—recent Australian literature

We focus on N transformations in freshwater sediment systems—in rivers, lakes, and reservoirs (wetlands are dealt with separately by Darren Baldwin). The broad outlines of the biogeochemistry of freshwater sediment dynamics are reasonably well understood (see eg. Fenchel et al., 1998). The earlier literature on nitrification is comprehensively reviewed by Howarth et al. (1988a,b). Denitrification is summarised in the companion article by Seitzinger (1988).

There was only a limited amount of published work dealing with N transformations in Australian freshwater sediments. Nitrogen transformations in cognate systems such as macrophytes, periphyton, and hyporheos were equally scarce. Among the few relevant papers, Qiu and McComb (1996) reported on the consequences of wetting and drying on nitrification and ammonia release rates in sediments. Eyre and Twigg (1997) described the dissolved inorganic nitrogen (DIN) dynamics in the freshwater part of an estuary. This slender harvest was in marked contrast to the numerous papers dealing with all aspects of N cycling, but with special emphasis on N removal, in sewage treatment lagoons and in wetlands. While some fruitful insights for natural freshwater systems and reservoirs flow from this work (as we show later), the high concentrations of the different N species and of reactive organic matter make it of limited relevance to the behaviour of quasi-natural systems.

The workshop organisers asked us to identify significant international work which addressed the ‘big questions’. In the following section we set out this broader perspective, together with germane Australian work in progress.

International perspectives and work in progress

Mirroring the Australian experience outlined above there is relatively little international effort (vis-à-vis phosphate) going into N transformations in freshwater sediments. In our view the most exciting and relevant work aims to quantify individual processes and thus provide a basis for integrated models of N and phosphorus cycling in freshwater systems and thus facilitate improvements in management. We list below some notable recent examples relevant to the Australian aquatic environment.

Role of microphytobenthos

In contrast to marine systems (see Brett Light’s talk) the biogeochemical role of the freshwater microphyto-benthos/benthic microphytos is a little researched topic. The recent development of novel microelectrode techniques has made possible the detailed investigation of the spatial distribution of both oxygen and nitrate in a very thin diatom layer on freshwater sediments (Lorenzen et al., 1998). This work showed close coupling between nitrification and denitrification in the illuminated diatom layer, and yielded rates of nitrification and denitrification. In the dark, there was no nitrification, and the denitrification rate was reduced by a factor of 10 relative to the illuminated case. In the Goulburn River we have found high sediment Chl *a* and benthic oxygen production: both symptomatic of diatoms (Bourgues, Ford, Grace and Hart, unpublished data).

These findings have possible important implications for Australian freshwater systems: control of ammonia/nitrate fluxes through water turbidity (determined by flow) limiting the depth of light penetration; and marked differences in fluxes between day and night. Consequently, daily net fluxes may differ significantly from shorter term measurements, and dark chamber results will differ markedly from illuminated chambers. Diurnal cycles of DIN uptake and release have been seen in field observations of a shallow estuary (Webster, Ford and Hodgson, unpublished data). Risgaard et al. (1994) demonstrated diurnal variation in nitrification and denitrification in laboratory cores taken from freshwater and estuarine sediments.

Modelling N cycling in sediments

Numerical models which quantify the coupling between N transformations and transfer in sediments are now well established. They are used to predict nutrient profiles and fluxes during marine sediment diagenesis (Blackburn and Blackburn, 1992). Variants of these models have been devised for freshwater environments (Mike Harper, Ian Webster, and Yunhu Tan, pers. comm.). They have the potential to illuminate aspects of N-cycling where the spatial or temporal scales preclude experimental measurement, or where the necessary technology, ie. ammonia microelectrodes, does not exist. There are now modelling groups at Monash and CSIRO Land and Water.

Biofilms and hyporheic flow

Extensive nitrification and denitrification within the sediments of low-order streams has been demonstrated and shown to involve hyporheic flows not just diffusive exchanges with the bed (Triska et al., 1993). These N transformations take place within the biofilms covering the surface of the coarse-grained sediments in the stream-bed. Recent investigations of nitrifying biofilms (Schramm et al., 1996), using both microelectrode and sophisticated molecular biological techniques, have measured the rates of the various processes as well as the spatial distribution of the bacterial species involved in the different steps. With extensive sand layers in rivers in the Murray–Darling Basin (Jon Olley, pers. comm.) these findings suggest that the hyporheic component may be a significant factor in the overall N dynamics of lowland Australian rivers.

Nitrification, and nitrate uptake in freshwater systems—sediment, littoral, or pelagic dominated processes?

Several data sets (Table 1) suggest that oxic sediments are sinks for nitrate and sources of ammonia to the water column. As the water-column ammonia is usually low, the released ammonia must be nitrified within the water column, usually in the hypolimnetic portion (Hall, 1982). It is not clear whether this occurs actually in the dissolved phase or on resuspended particles. In the freshwater portion of the Elbe (Stehr et al., 1995) the ammonia oxidising activity was totally in the suspended particles and these would be expected to be concentrated at depth in stratified systems (Condie and Bormans, 1997). In our work in the Fitzroy River Barrage near Rockhampton, the measured sediment nitrate fluxes are insufficient to account for the observed rates of removal of nitrate from the water column, therefore requiring another sink elsewhere. The profiles of nitrate (Figure 1) show a source of nitrate in the aerobic hypolimnion and a sink in the surface layer. This suggests that the periphyton and the abundant biofilms in the adjoining wetland and attached to para grass in the surface layer act as the nitrate sinks. This is consistent with Axler and Reuter's (1996) conclusion that periphyton nitrate uptake and denitrification were the principal sinks for water column nitrate.

Table 1. Fluxes of nitrate and ammonia in oxic sediments (negative sign indicates fluxes into the sediment). Darkened chambers were used in all cases

Location	Nitrate flux (mM m^{-2} day^{-1})	Ammonia flux (mM m^{-2} day^{-1})
Fitzroy River Barrage, Qld	–0.04	0.03
Goulburn River, Vic.	–1.4 to + 1.9	0.5 to 5.0

If generally applicable, these results have implications for the management of Australian water bodies. Nitrate concentrations in rivers and lakes will depend on exchanges between the littoral, wetlands, and the water body proper, as well as water column processes determined by temperature and mixing/stratification. In terms of providing surface area to support denitrifying biofilms, 10 insignificant (1 cm diameter) macrophytes will provide the same surface area as a 10 cm snag of the same wetted length.

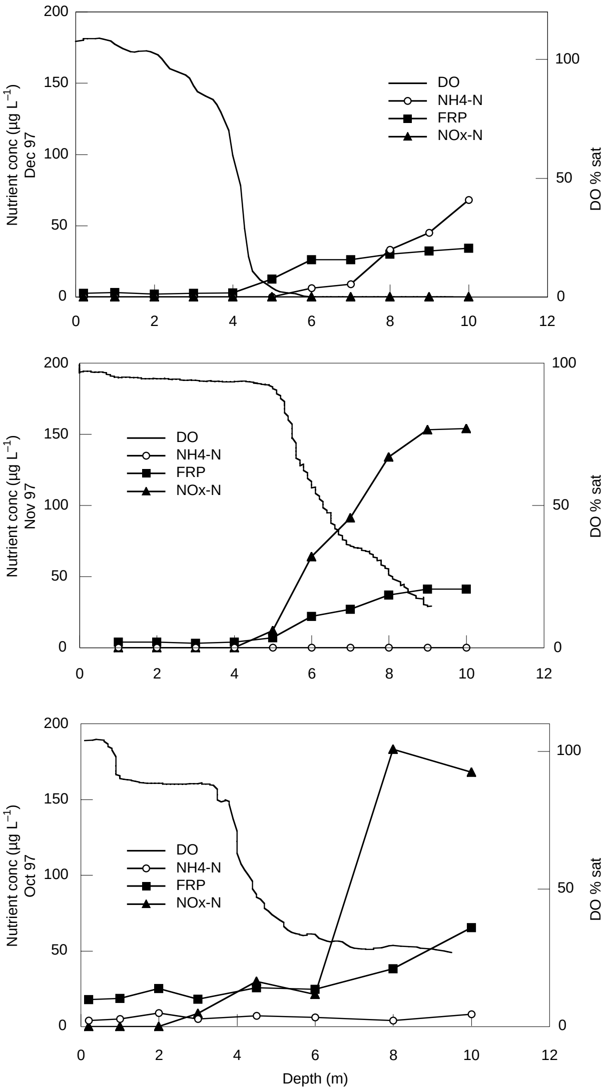

Figure 1. Nutrients and dissolved oxygen profiles in the Fitzroy River Barrage, Queensland

Temperature dependence of nitrification and denitrification

Denitrification within sediments is coupled to diagenesis of organic matter to produce ammonia, and the subsequent nitrification of ammonia. The relative rates of the three processes will determine the denitrification efficiency of the sediments, and the source/sink strength for all three species of DIN. In marine systems, the three processes have been shown to be highly temperature dependent (Nixon et al., 1976; Berounsky and Nixon, 1990; Nowicki 1994). The situation for freshwater sediments has not been investigated. We have observed a pronounced seasonal oscillation in ammonia concentration (Figure 2) in sewage treatment ponds at Albury, NSW (Ford and Donnelly, unpublished data). A similar seasonality is apparent in Figures 1–3 of Peter Breen's paper in this volume. The ammonia and nitrate concentrations are inversely correlated, and the total DIN is lower in summer. All three observations suggest that nitrification and denitrification rates are highly temperature dependent in freshwater systems also. If generally valid, this suggestion has important implications for the behaviour of Australian freshwater sediments: in temperate systems there will be marked seasonal differences in rates of ammonia and nitrate production, and denitrification efficiency Winter floods will deliver proportionately more ammonia than nitrate to estuaries. The proportions will be reversed in summer floods. In warmer tropical systems, nitrification and denitrification will be much faster and the concentrations of all three DIN species will be much reduced, leading to a conditions favourable to N-fixing cyanobacteria.

Techniques

The isotope ratio method (Nielsen, 1992) and the acetylene block method are the standard methods for

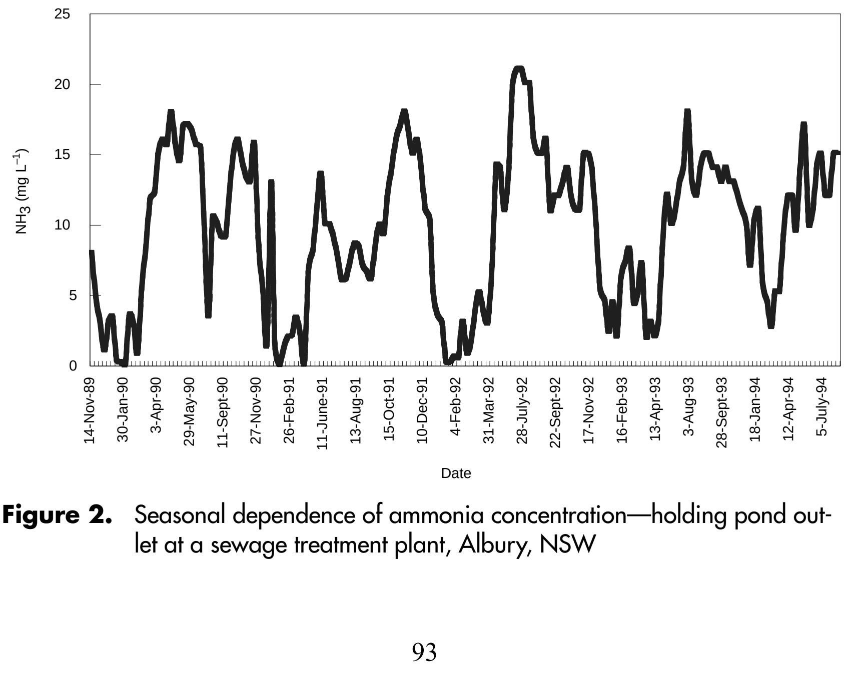

Figure 2. Seasonal dependence of ammonia concentration—holding pond outlet at a sewage treatment plant, Albury, NSW

assessing nitrification/denitrification and N fixation in sediments. They are best applied in cores recovered from the field: they require specialised skills and equipment, and they are not artefact free (Seitzinger et al., 1993). The recent development of membrane inlet mass spectrometry (MIMS) (Kana et al., 1998) promises to revolutionise the study of N cycling in both freshwater and marine sediments. There are now two such machines in Australia (AGSO – Dave Fredericks and SCU – Brad Eyre) and Monash University is developing a home-grown version. Coupled nitrification and denitrification can be estimated from the same benthic chamber simultaneously with measurement of O_2 production or uptake, as well as the liberation of other gases such as methane and N_2O. Nitrogen fixation can be measured also. Extension of the methodology to an isotope ratio machine would greatly assist identification of the N source.

Role of flow and stream dimensions

Very recent work (Alexander et al., 2000) suggests that the N loss rate declines rapidly with increasing channel size. This is consistent with spatial variation of nitrification, if nitrification is primarily a water column process, while denitrification takes place on the sediment surface and in biofilms. Flow rates, and the presence or absence of hyporheic flow, can be expected to affect the rates of removal of DIN from the water column also. This has implications for the delivery of N to estuaries. Progress in understanding these effects requires an integration of the hydrodynamic and biogeochemical factors.

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Nitrogen cycling: microbial processes

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Bacteria and the nitrogen cycle

Bacteria are generally considered only as decomposers in aquatic systems, regenerating nutrients from dissolved and particulate detritus. This is a very limited view, as bacterial growth and related assimilation of nitrogen (N) creates a substantial nutrient demand. Indeed, bacteria can be strong competitors (with algae and macrophytes) for nutrients. A narrow view of bacterial function also fails to consider the vital role that bacteria play in transforming different forms of N; processes such as N fixation, deamination, nitrification and denitrification are entirely bacterial in nature. In this review, I concentrate on bacterial activities relevant to N cycling in Australian coastal marine systems: research is far more advanced in this environment than in comparable freshwater environments. The principles, methods and results, however, are easily transferable to freshwater systems, especially to wetlands and other lentic water bodies.

Bacterial productivity and whole-ecosystem nitrogen demands

The biomass of bacteria is substantial in many freshwater systems (eg. up to 10 mg C L^{-1} in the water column of billabongs: Boon (1991)) and given the potential for bacteria to have short division times (< 2 hours: Moriarty and Boon (1989) and Boon (1991)), bacteria may be significant sources of aquatic secondary production. In some cases, bacterial productivity approaches the primary production of the algae and/or macrophytes. Tropical seagrasses provide an example: bacterial secondary production accounts for at least 10–30% of the production of the plants (Moriarty and Boon, 1989).

High rates of bacterial production would have little significance for aquatic N cycling if the bacteria had a low N content. Bacterial biomass, however, is largely comprised of N-rich polymers, such as protein (55% of dry weight) and RNA (21% of dry weight); the C:N ratio of bacteria is commonly about 3:1 to 5:1. Rapid growth combined with a low cellular C:N ratios translate to a very high bacterial N demand.

Although the N demands of macrophytes and algae have been quantified frequently, there is little empirical information on the demand for N created by bacterial assimilation. A quick-and-nasty calculation using an Australian seagrass-bed example shows that the bacterial demands for N may approach the macrophyte demands. The N demand of *Zostera capricorni* in Moreton Bay has been calculated at 61 mg N m^{-2} day^{-1} (Boon 1986b; Moriarty and Boon 1989). The production of the aerobic bacteria, measured by the rate of ^{3}H-thymidine incorporation into DNA, was about 80 mg C m^{-2} day^{-1} (Moriarty et al., 1985). The production of anaerobic bacteria (mainly sulfate-reducers) was probably at least as great. Thus, the N demand required to satisfy bacterial growth in the seagrass bed sediments and water column must have been about 30–50 mgN m^{-2} day^{-1}.

Bacterial transformations of nitrogen

As well as having an important function in assimilating N, bacteria play central roles in transforming the various types of N in aquatic systems. Examples include the following:

Nitrogen fixation

The conversion of N_2 to amino acids is an ability possessed only by prokaryotes. Nitrogen fixation can be undertaken by some groups of cyanobacteria (blue–green algae), such as *Anabaena*, as well by as a wide range of heterotrophic bacteria. The heterotrophic bacteria are usually closely associated with higher plants, either in a symbiotic relationship (eg. *Rhizobium* with terrestrial legumes) and as a looser interaction in the rhizosphere or phyllosphere (eg. *Clostridium*, *Klebsiella*, *Desulfovibrio*, *Methylococcus* etc.). The N-fixing ability of aquatic ferns, such as *Azolla*, resides in cyanobacteria inhabiting cavities on the underside of the sporophyte thallus. The close relationship between N-fixing bacteria and plants is probably a function of the energetic cost of breaking the triple bond in the N_2 molecule: plants ‘provide’ the photosynthate required as the energy source for the fixation process. Nitrogen fixation can provide significant amounts of N for the host plant; in tropical seagrass beds from 8–16% of the daily community (ie. seagrass plus bacteria) N requirement is met by N fixation (Moriarty and O'Donahue, 1993).

Deamination

Deamination is the conversion of amino acids to ammonium during the process of organic-matter decay. In freshwater systems it is almost totally the province of bacteria. Fungi may have a role in some semi-terrestrial systems and on submerged decaying leaves, but we have failed to detect the presence of fungi (using the sterol biomarker, ergosterol) in any of our wetlands (Boon et al., 1996).

Nitrification

Nitrification is the conversion of ammonium to nitrite, and nitrite to nitrate. It is usually an autotrophic process, undertaken by bacteria in order to obtain the energy required to fix atmospheric carbon dioxide. The oxidation requires the presence of abundant free O_2, since the bacteria are obligate aerobes. There have been some reports of nitrification being undertaken by heterotrophic organisms (eg. fungi) but the autotrophic route is likely to dominate overwhelmingly in aquatic systems. In the published literature, emphasis is given to two genera of nitrifying bacteria—*Nitrosomonas* and *Nitrobacter*—because they are the taxa isolated most commonly from the environment. This may, however, be an artifact of plating methodology and it is not clear that *Nitrosomonas* or *Nitrobacter* really are the most important (or abundant) taxa under natural conditions.

Although nitrifying bacteria are often slow growing (generation times of 20–40 hours), they can cause significant depletions of dissolved oxygen in the water column, and account for a major component of the biological oxygen demand of the sediments. Moreover, the energetics of CO_2 fixation using ammonium or nitrite as energy source is such that *Nitrosomonas* uses about 35 NH_4^+ and *Nitrobacter* about 100 NO_{2-} per CO_2 fixed. Thus, the nitrifiers make not only appreciable demands on O_2 supply, but also on N supplies; these demands are seemingly out of proportion to their apparent small biomass and slow growth (Sprent, 1987).

Denitrification

Denitrification is the dissimilatory reduction of nitrate (or nitrite) to the gases N_2O or N_2. It is a process undertaken by a very wide group of facultative anaerobic bacteria that use nitrate as an alternative electron acceptor when O_2 becomes unavailable. Although denitrification is thought to occur only under anaerobic conditions, there have been recent, credible reports of aerobic denitrification in sewage ponds. In any case, the poor diffusion of oxygen in aqueous media means that denitrification can occur, in anaerobic microsites, even in apparently aerobic systems (eg. with DO > 4 mg L^{-1}: see Boon (1986a)).

The growth efficiency of denitrifying bacteria is very high in comparison with other anaerobic microbes, and approaches that of the aerobic bacteria, since nitrate is an excellent oxidant ($\Delta G'_o = -560$ kJ mol^{-1} for nitrate reduction: cf. –235 kJ mol^{-1} for sulfate reduction and –61 kJ mol^{-1} for methane production). Accordingly, denitrifying bacteria can degrade a wide range of organic materials, including complex biopolymers such as DNA and protein. (Note that other anaerobic bacteria, eg. sulfate reducers and methanogens, are very limited in the range of carbon substrates that they can metabolise.) At least 73 taxa of bacteria undertake dissimilatory reduction of nitrate to nitrite, and about 25 taxa take the reaction through to its final phase and produce the gaseous end-products N_2O or N_2 (Sprent, 1987).

Dissimilatory reduction to ammonium (DRA)

The dissimilatory reduction of nitrate to ammonium, rather than to N gas, is found under the same environmental conditions as denitrification. It tends to be favoured over denitrification when the redox potential is very negative and organic carbon is freely available. Nevertheless, we have detected DRA in well-aerated sandy coastal sediments (Boon et al., 1986b). The physiological significance of DRA is that it is an energetically very favourable way of using any nitrate that might occur in anoxic sediments. The ecological significance of DRA is that it conserves N within a habitat: denitrification results in the net loss of bioavailable N from a system, and that can only be 'made good' by the costly process of N fixation.

Filling knowledge gaps using new methods

Advances in environmental microbiology are intimately associated with technical developments, and there is a huge literature on methods suitable for studying microbes in their natural environments (eg. Boon, 2000). Here I touch on three approaches that have potential for filling some of the existing knowledge gaps in the microbial aspects of N cycling.

Molecular probes

Traditional microbiological methods (eg. plate counts and isolation of pure cultures) offer little to environmental microbiology. In contrast, modern molecular methods have the potential to revolutionise our understanding of the functioning of natural ecosystem. To date, the most productive method has been analyses of 16S rRNA: this has allowed the construction of taxa-specific oligonucleotide probes for in situ identification and enumeration of specific bacterial groups on a phylogenetic basis, such as methanotrophs and nitrifiers (Ross et al., 1997). In principle, DNA approaches permit the identification and enumeration of key physiological groups (such as denitrifiers) on the basis of their possession of specific gene sequences (Boon, 2000).

Selective inhibitors

Because bacteria are prokaryotic, they have membrane structure, cell wall structure and protein metabolism that are markedly different from eukaryotic organisms. Accordingly, selective compounds have found great use in selectively inhibiting the bacterial component: the use of antibiotics in human disease is the most obvious example. There are several specific inhibitors than can be used to study bacterial activities in the aquatic N cycle. Antibiotics are commonly used to selectively inhibit the bacterial component in leaf-decay studies: rarely is this usage effective, despite the best hopes of the researcher (Boon, 1992; Boon and Cattanach, 1999). Conversely, cyclohexamide can be used to inhibit eukaryotes in aquatic systems.

Some substances are useful in selectively inhibiting a particular group of bacteria. For example, 2-bromo-ethanesulfonic acid (BES) is a structural analogue of mercaptoethanesulfonic acid, the cofactor known as HS-coenzyme M in methanogenic bacteria. It inhibits methane production at concentrations of 10^{-4} to 10^{-5}M. Molybdate and other Group VI elements selectively inhibit sulfate-reducing bacteria. Because the inhibition is competitive, higher concentrations are required in marine (ca. 28 mM sulfate) than in freshwater (< 1 mM sulfate) systems.

Other substances can be used to inhibit specific components of the N cycle. Although the presence of O_2 nominally inhibits denitrification (and nitrification ceases in the absence of O_2), manipulating oxygen regimes to selectively inhibit one or the other process creates such gross changes in redox that rarely are the outcomes selective. Nitrapyrin (N-serve) selectively inhibits autotrophic nitrification, but its use in aquatic systems is limited severely by it being poorly water soluble (Boon, 1986a). It can be used either in concert with analyses of ammonium or nitrate dynamics or with [^{14}C] bicarbonate uptake. Allylthiourea, at concentrations from 10–100 mg L^{-1}, probably offers more potential as a selective nitrification inhibitor (Hall and Jeffries, 1984). Acetylene (at about 0.1 atm or greater concentrations) is widely used as an assay for N fixation and for denitrification, in the latter since it prevents the final conversion of N_2O to N_2. Sadly, acetylene also inhibits a wide range of microbial processes and it cannot really be considered a selective inhibitor. For example, in addition to inhibiting N_2O-reductase (hence its use in measuring denitrification) it also inhibits nitrification (and so the production of nitrate), and this has severe implications when low-nitrate sediments are studied.

It is easy to see that results from inhibitor studies usually have more than one interpretation, and usage of some inhibitors will generate results that are difficult to explain. Often, the inhibition that is achieved in natural systems is neither as rapid nor as complete as one might like; poor specificity is also quite common, despite the putatively ‘selective’ nature of the inhibitor.

Stable isotope analyses

Nitrogen has two stable isotopes (^{14}N and ^{15}N) as well as a number of very short-lived radioactive isotopes. Of the two stable isotopes, ^{14}N is far more abundant and accounts for more than 99.5% of the total N pool. The radioisotopes have too short a half-life (< 10 minutes) to be generally useful in ecological studies, although some research has been conducted by workers with immediate access to cyclotrons.

Stable isotopes can be used in two ways to study N cycling. The first involves the use of nitrogenous compounds artificially enriched in ^{15}N (up to 99% ^{15}N compared with the ca. 0.4% ^{15}N occurring naturally) to trace N transformations. For example, we have used highly enriched $^{15}N\text{–}NO_3^-$ to measure the fate of nitrate in marine sediments (ie. denitrification and DRA: Boon et al., 1986b). An exciting use of ^{15}N is to quantify the turnover of interstitial pools of ammonium, via the progressive dilution of added $^{15}N\text{–}NH_4^+$ with newly regenerated (and therefore ^{14}N) ammonium mineralised from in situ organic matter (Blackburn, 1979). We have used the isotope dilution approach to show that interstitial pools of ammonium in seagrass bed sediments turned over every 0.4 to 0.8 days (Boon et al., 1986a), in close agreement with values obtained from field calculations (Boon, 1986b). Another use of ^{15}N is in the determination of deamination rates, using ^{15}N–labelled amino acids: we have shown that 35–65% of added ^{15}N-glycine was converted daily to ammonium in seagrass-bed sediments (Boon et al., 1986a).

The general limitation to the ^{15}N methods is the poor sensitivity of mass spectrometry (in comparison with scintillation counting for radioisotopes) for the tracer and the subsequent necessity to use quite large additions of the labelled compound, making them a ‘non-tracer’ addition. Alternative instrumental techniques, such as emission spectroscopy, offer a solution to this problem, but do not have mass spectrometry’s ability to finely resolve isotope ratios near natural enrichments. Their preparatory steps are also very laborious.

The second isotopic approach is to examine natural variations in the ratio between ^{14}N and ^{15}N (called δ^{15}N). In terms of absolute abundance, ^{15}N accounts for a slightly variable amount of the total N in a sample, commonly between 0.362 and 0.372%, or in delta terminology, an isotopic signature of –10 to +15 ^{o}/oo. Since there is isotopic fractionation at each biochemical transformation in the N cycle and additional fractionation caused by biophysical events (eg. a result of diffusional differences in the two isotopes), there is often a pattern to these subtle changes in natural isotope ratios (Lajtha and Michener, 1994).

The processes that are best studied by quantifying isotopic variations are either processes with:

- •high fluxes and slight fractionation (eg. mineralisation, nitrification and N fixation), or
- •large fractionation but smaller fluxes (eg, ammonium volatilisation and denitrification).

For example, the N signature of plants obtaining their N from N_2 fixation is commonly 0 to –2^{o}/oo (ie. that of atmospheric N). In contrast, plants obtaining their N from NO_{3-} in fertilisers often have $\delta^{15}N$ signatures of +2 to +4 ^{o}/oo. This usage is analogous to that of the stable isotopes of carbon ^{12}C and ^{13}C ($\delta^{13}C$) in tracing carbon fluxes in food webs (eg. Bunn and Boon, 1993).

Recent activities in our laboratory

Since 1998, we (Paul Boon at VU and Paul Bailey at Monash University) have been supported by the National Wetlands R&D Program to investigate the effects of nutrient enrichment on primary production in shallow freshwater wetlands. Three approaches have been used:

- •large (12 m × 12 m) replicated mesocosms dug into in an ephemeral wetland on the floodplain of the Goulburn River near Shepparton, central Victoria, and the sediments dosed with a slow-release fertiliser;
- •smaller (2 m diameter) replicated mesocosms in a shallow urban wetland heavily colonised by submerged macrophytes, especially *Vallisneria gigantea*, and the water column dosed at over a wide range of nutrient concentrations with both rapid- and slow-release fertiliser; and
- •focused laboratory experiments on the ability of wetland sediments (and their microbiota) to take up and transform N and phosphorus.

Key results from these experiments were outlined during the workshop presentation.

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Nitrogen cycling in Australian wetlands — a synthesis

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Worldwide, the study of nutrient cycling in wetlands (particularly nitrogen, N) is of considerable interest, primarily because of the increasing use of constructed wetlands for water treatment.[1] However, there is relatively little research on N dynamics in freshwater wetlands in this country. In this paper, we will initially present a quick overview of the key components of the N cycle in aquatic ecosystems in general and then examine how these processes are affected by the special conditions found in wetlands. Finally, we would like to highlight knowledge gaps and areas for future research.

N cycle in aquatic systems

A stylised version of the aquatic N cycle is presented in Figure 1.[2] Nitrogen can enter an aquatic system through a number of pathways including:

- as part of either living or dead biomass (‘organic N);
- through fixation of N_2 gas;
- from anthropogenic inputs (including point-source and non point-source pollution);
- from aerial deposition; and
- from groundwater sources.

Once in an aquatic system, the N can undergo a number of transformations. Like most aquatic biogeochemical cycles, the cycling of N is predominantly mediated by the microbiota—although there is some evidence that mineral phases such as Mn may play some role (Luther et al., 1997). Furthermore, like the other cycles, different reactions occur under oxic and anoxic conditions.

In the oxic zone, ammonia—produced through the mineralisation of dissolved organic N—can be converted to nitrate (via nitrite) by bacterial action, ie. nitrification. The ammonia can also either be taken up by bacteria, algae and/or macrophytes or, if the pH is sufficiently high, lost to the atmosphere through volatilisation (Reddy and Patrick, 1986). In the anoxic part of the sediment, nitrate can either be reduced back to ammonia (dissimilatory nitrate reduction to ammonia) or converted to nitrogen gas (de-nitrification). Dissimilatory nitrate reduction to ammonia (DNRA) preserves N in the system. Because N_2 gas has a low solubility in water, denitrification is a pathway for the removal of nitrogen from aquatic systems. This is particularly important if nitrification and denitrification are coupled (ie. the two processes occur spatially close to each other), as the nitrate produced in nitrification can be quickly converted to nitrogen gas rather than being assimilated into biomass. Coupled nitrification–denitrification has to occur at the boundary of oxic and anoxic environments.

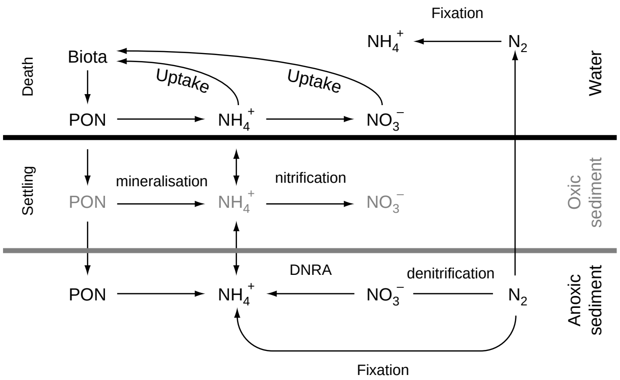

Figure 1. Stylised N cycle (after Rysgaard, 1993)

Wetland characteristics that impact on N cycling

Wetlands by their nature have a number of characteristics that can influence the relative importance of various processes within the N cycle.

1. A literature search of the Science Citation Index found ca. 500 papers published between 1993–2000 using the key words ‘nitrogen AND wetland’. Almost half of these were on constructed wetlands.

2. We have included only end members of each pathway and therefore we have not included intermediates such as NO_2 and N_2O in the scheme. Obviously they are important in N cycling.

Wetlands as deposition zones

Wetlands are often found at the terminus of a flow pathway. Consequently, they are characterised by generally having low flows relative to the watercourses that feed them. As such, terminal wetlands act as zones where fine suspended materials (including suspended sediments and particulate organic matter) are deposited. Therefore, the bed sediments of wetlands are often very fine and rich in organic matter. This combination of reduced flow, lack of sediment porosity and high organic matter load results in sediments that tend to be devoid of oxygen; facilitating anaerobic processes such as denitrification and dissimilatory nitrate reduction to ammonia.

The rhizosphere

Although wetland sediments tend to be anoxic, many wetlands support a variety of submerged and emergent macrophytes whose root systems extend into the anoxic muds. To survive, these root systems require a supply of oxygen. Many wetland macrophytes have evolved both active and passive mechanisms to transport oxygen to their root systems (Reddy et al., 1989; Boon and Sorrell, 1991). Oxygen leaking from the roots creates a zone of oxic sediment close to the root surface. Therefore, the sediment under stands of macrophytes will have zones of oxidised sediment threading through the predominantly anoxic sediment (Reddy et al., 1989). The juxtaposition of oxic and anoxic zones favours coupled nitrification–denitrification. Indeed, Reddy et al. (1989) see the rhizosphere as probably the most important site for denitrification in wetlands as a direct consequence of the continual supply of nitrate from nitrification. Carbon may also leach from the macrophyte biomass—enhancing microbial activity.

Biofilms on emergent and submerged macrophytes.

Another potential site of coupled nitrification – denitrification is within biofilms[3]. Biofilms are complex assemblages of algae and bacteria that form on solid substratum. It has been shown that substantial quantities of biofilms can form in wetlands on the submerged stems of macrophytes. Indeed, using isotope-pairing techniques in mesocosms, Erikson and Weisner (1999) suggest that epiphytic bacteria account for a substantial amount of the measured nitrification. However, those authors found no evidence of coupled nitrification–denitrification; denitrification occurred only in the sediments. This contrasts with an earlier study by the same authors (Eriksson and Weisner, 1997) which showed the major pathway for N removal in a shallow municipal storage receiving municipal waste was denitrification by epiphytic microbial communities growing on submerged vegetation. Despite these contradictions, it is clear that epiphytic bacterial assemblages may be important in N cycling in wetlands.

3. Including biofilms growing in hyperheic zones of rivers.

Groundwater

Some wetlands receive most of their water from groundwater inflows. In some places the groundwater can contain very high levels of nitrate (with values significantly greater than 10 mg/L being not uncommon.) Previously we have shown that denitrification in a water storage reservoir was nitrate limited (Mitchell and Baldwin 1999). Therefore, wetlands with nitrate-rich groundwaters may have high rates of denitrification (and therefore be significant contributors of the greenhouse gas N_2O to the atmosphere).

High pH

Wetlands are often sites of high primary production. As a consequence, during the warmer months, the pH of some wetlands can become quite alkaline—more so than many water bodies. Daytime pH levels greater than 10.5 are not uncommon in wetlands such as Ryan’s 1 and 2 during the summer months (R. Sheil, pers. comm.). The highly alkaline water can lead to the volatilisation of ammonia. The pK_a for the equilibrium

$$NH_3 + H^+ \leftrightarrow NH_4^+$$

is 9.24. That means at pH 9.24, half of the ammonia would be as ammonia gas and half would be protonated to form the ammonium ion. At pH of less than about 8, almost all the ammonia would be as NH_4^+, while at pH greater than about 10.5 it would be almost all NH_3. Therefore, net ammonia loss can occur from these systems during summer.

Wetting and drying

Many wetlands are ephemeral—undergoing periodic drying. The impact of drying on N cycling in wetlands is potentially quite complex (Baldwin and Mitchell, 2000). Probably the most important impact of desiccation on N cycling is the death/senescence of both plant and microbial biomass.

On rewetting, a pulse of nutrients, previously locked up in microbial biomass, is released to the water column (Birch, 1960; Qiu and McComb, 1996). Macrophytes will compete with bacteria for the nutrients flushed on rewetting (Bodelier et al. 1998). Increased plant productivity and uptake of the nutrient pulse following the rewetting of desiccated soils has been reported for emergent macrophytes (eg. Cui and Caldwell 1997). In contrast, the response of submerged aquatic macrophytes will vary depending on the severity of the drought

(Hough et al., 1991) and the plant species present (Brock and Casanova 1997). However, the N is most likely to be used by the microbial consortia in wetland sediments (Vegasvilarrubia and Herrera 1993). It would appear that wetland bacteria adapt to extended periods of desiccation and can react to rewetting (Kern et al., 1996; Mitchell and Baldwin, 1999).

Australian research

A search of the literature between 1993 and the present[4] found 29 reference on N cycling in wetlands. Eighteen of the references dealt either with constructed wetlands and/or the use of wetlands for polishing wastewater. Indeed, only three papers (Greenway, 1994; Qiu and McComb, 1996; Raisin et al. 1999) dealt with N cycling in natural wetlands not used for wastewater treatment. (The remaining articles covered aspects of N cycling in agricultural systems or reservoirs.) Taking a lead from Boon and Brock (1994), who suggested that much of the extant work on wetlands may go unreported in the scientific literature, we posted a request on the Australian Society for Limnology (ASL) server for anybody doing research on N cycling in wetlands to contact us. Based on the literature survey and the responses from the ASL request, we constructed the following list of people/groups who have been active in researching N dynamics in freshwater wetlands over the past 7 years. (In all probability we have excluded a number of researchers from the list so, it should not be seen as exhaustive. Current projects are marked with an asterisk.)

- D. Baldwin (Cooperative Research Centre for Freshwater Ecology) – nutrient cycling in anaerobic wetland sediments*
- J. Bavour (University of Western Sydney) – constructed wetlands for pollution control*
- A. Boulton (University of New England) – N cycling in the hyperheic zone of temporary streams*
- P. Breen (Cooperative Research Centre for Freshwater Ecology) – vertical flow wetlands
- M. Greenway (Griffith University) – constructed wetlands for treating wastewater*
- A. Heritage, I. Lantske et al. (CSIRO Land and Water) – constructed wetlands
- R. Johnstone (Australian Water Technologies) – denitrification in coastal wetlands*
- A. Mitchell (Cooperative Research Centre for Freshwater Ecology) – interaction of anaerobic geochemical cycles*
- D. Mitchell (Charles Sturt University) – constructed wetlands for treating grey-water.
- S. Qiu & A. McComb (Murdoch University) – Wetting/drying and nutrient cycling
- G. Raisin (Department of Land and Water Conservation) – Wetlands for ameliorating diffuse pollutant loads
- G. Rees (CRC for Freshwater Ecology) – nitrogen fixation in wetlands*
- A. Waite (University of Western Australia)*– nutrient dynamics in the Canning River
- B. Wilson (Charles Sturt University) – occluded ammonia in wetland sediments*

4. Scientific Citation Index sing the key words 'Nitrogen and Wetland' as topics and Australia as the address.

Future directions

From the paucity of research into N cycling in wetlands in this country, it can be concluded that we have large knowledge gaps with respect to N cycling in wetlands. In particular we do not have good estimates on the rates of key processes (although some rate data can be inferred from load estimates). Furthermore, and we believe of much greater importance, we do not understand how the N cycle interrelates to other bio-geochemical cycles occurring in wetlands, nor do we understand how shifts in processes such as N cycles in wetlands impacts on the ecology and biodiversity of the system.

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Biogeochemical modelling of water column transformations and fluxes of nitrogen

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Introduction

Quantitative modelling of the fluxes and transformations of nitrogen (N) is complicated by three main factors. First, although the large number of processes that influence transformations and speciation of N is understood conceptually, quantifying the rates at which these processes occur in the natural environment is still rudimentary. Second, mass balance studies that trace particulate and dissolved forms of material are complicated for N by the processes of volatilisation, denitrification and cyanobacterial fixation, which introduce interactions with atmospheric forms of N and may not be easy to separate. The third reason is a universal one and relates to the complexity of transport processes that influence the distributions of N species in the natural aquatic environment. These points indicate how any modelling approach for N is invariably a moderate-to-gross simplification of the processes involved and will therefore require calibration to compensate for inadequacies of model process representation and unknown transformation rates.

Rather than address all of the inadequacies and uncertainties in our conceptual and numerical modelling approach for N, I have chosen to examine several processes in detail. This serves to illustrate that while our conceptual understanding of N dynamics has advanced substantially in the past decade or so (see Harris, 1999), comparatively few data are available to comprehensively validate N kinetics in numerical models. Thus, simple mass balance modelling approaches are likely to continue to play a role in assessments of N fluxes, even if only to make preliminary assessments of net non-conservative (i.e. atmospheric) transformations of N as the 'unknown' term in the mass balance equation. Indeed, a suite of models may provide the best approach to encompass a variety of spatial and temporal scales to further our understanding of N fluxes. Further, acquisition of N distributions in the natural environment of finer temporal and spatial resolution in conjunction with automated sampling equipment will allow different levels of rigour in model calibration and validation. In this paper, I highlight three N transformation pathways, namely nitrogen fixation, denitrification, and nitrification, and describe the environmental factors that influence these pathways in Australian waters.

Mass budget approach

The application of a mass balance for N relies upon adequately quantifying the load to a selected domain. This domain can be an entire lake for standing waters, a selected section of river, an estuary, or a user-defined region for coastal embayments or the ocean. Clearly there is a gradation of increasing difficulty in quantifying mass fluxes across the boundaries from lakes to coastal seas. For simplicity and brevity, the focus here is primarily enclosed waters, such as lakes.

Surface and sub-surface flows are both sources and sinks of N, while atmospheric deposition via rainfall and particulate fallout can be an important source of N. Atmospheric sources of N are variable spatially and temporally, and unless regular monitoring is undertaken, this variability may complicate load calculations. Quantifying nutrient loads in inflows presents statistical difficulties when fixed time interval grab sampling is used (Donohue et al., 2000), especially in Australia with its extreme temporal variability of climate and hydrology. However, with improved sampling protocols, increased use of autosamplers and flow-weighted sampling, good estimates of nutrient loads can be attained, at least to standing waters. Further, though often neglected, diffuse sources of N should always be considered in mass balances, and may be especially important in groundwater dominated wetlands such as those of Western Australia. Substantial hydrological variability will also lead to changes in fluxes of nutrients between recently wetted sediments and the water column, or alter inputs of N from dried sediments to the water via subsurface transport (Qiu and McComb, 1996).

With inflow and outflow loads quantified, budget equations can be written for water column concentrations of three commonly measured nitrogen species, total nitrogen (TN), nitrate + nitrite (NO) and ammonium (NH):

$$\frac{\partial TN}{\partial t} = TN_i + F + R - TN_o - D - V - S \quad (1)$$

$$\frac{\partial NO}{\partial t} = NO_i + NI - NO_o - D - U_{NO} \quad (2)$$

$$\frac{\partial NH}{\partial t} = NH_i + M + R - NH_o - V - U_{NH} - NI \quad (3)$$

where subscripts *i* and *o* refer to inflows and outflows respectively, *D* is denitrification, *V* is volatilisation, *F* is N_2 fixation by cyanobacteria, *S* is net sedimentation of particulate N, *R* is dissolved N release from bottom sediments, *NI* is nitrification, *M* is ammonisation and U_{NO} and U_{NH} are uptake of nitrate and ammonium by algae and macrophytes. Equation 1 is essentially a modification of the well known 'Vollenweider' approach for TP, but with additional terms for the atmospheric transformations, *D*, *V* and *F* (see Smith et al., 1989). Extending this approach to shallow marine waters, however, is complicated by interactions of phytoplankton biomass and macrophytic epibenthos (Harris, 1999).

For a particular setting, judicious elimination of terms in equations 1–3 can potentially allow a single unknown term to be determined. For example, volatilisation is rarely important unless concentrations of ammonia and pH are high (see Jayaweera and Mikkelson, 1990), and I do not address this process further here. Also, nitrogen fixation can be ignored unless there is a substantial biomass of N-fixing cyanobacteria. Alternatively, transformations of *N* associated with *D*, *V* and *F* may potentially be pooled to provide an estimate of the flux associated with non-conservative transformations of N. The time step *t* may be selected to provide mass balances at time intervals corresponding to the frequency of sampling or at longer intervals so that seasonal or inter-annual variations in certain processes may be elucidated.

Nitrogen fixation

Nitrogen fixation by certain species of cyanobacteria has the potential to generate large inputs of organic N and, through subsequent transformations, inorganic N, to aquatic ecosystems (Howarth et al., 1988). For example, 81% of the annual total N input to a high altitude hyposaline lake in the United States was contributed by the N-fixing cyanobacterium *Nodularia spumigena* (Horne and Galat, 1985). Also, Ganf and Horne (1975) recorded in situ N-fixation rates of up to 0.93 $\mu g\ L^{-1}\ hr^{-1}$ by several species of heterocystous cyanobacteria. A paucity of research has been conducted to quantify N fixation inputs to waterbodies in Australia, despite the prevalence of cyanobacterial blooms in this country (see Jones, 1994), perhaps as a result of the paradigm that phosphorus limits primary production in inland waters.

In freshwaters, almost all N-fixation is through heterocystous cyanobacteria. By contrast, there are few marine cyanobacteria with heterocysts, although heterocystous *Nodularia spumigena* is characteristic of moderately saline waters. Only the non-heterocystous *Trichodesmium* appears to be capable of N fixation at levels that may subsequently increase the availability of inorganic N in marine systems, but its contribution to marine N may still be substantial on a global scale. Nitrogen fixation requires an anaerobic environment and is an energetically expensive process (Van Baalen, 1987), as indicated by the utilisation of ATP in the general equation for N-fixation:

$$N_2 + 4NADPH + 6H^+ + 12ATP \rightarrow 2NH4^+ + H_2 + 12ADP + NADP^+ \quad (4)$$

Presumably because of the energy requirements, most N fixation in heterocystous cyanobacteria occurs during daylight hours and growth rates are typically reduced by around 30% compared to those in NH_4-saturated conditions. In non-heterocystous N-fixing cyanobacteria, there appears to be both an anatomical and temporal separation of dissolved oxygen from N-fixation and it is noteworthy that rates of N-fixation by non-heterocystous cyanobacteria are significantly greater at night or under anoxic conditions (Gallon and Stal, 1992).

The above discussion highlights several important facets of nitrogen fixation relevant to numerical modelling or predictive understanding of nitrogen fluxes. N fixation can potentially contribute significantly to N inputs to many Australian waterbodies. For example, N-fixing *Anabaena* and *Cylindrospermopsis* are important members of the phytoplankton flora of many Australian freshwaters, often those where artificial river regulation is imposed, but also natural lakes and wetlands. Interestingly, positive relationships have been established overseas between the presence of cyanobacteria and water residence times. These relationships need to be tested across Australian inland waters collectively, to quantitatively confirm the role of river regulation in cyanobacterial blooms. At present most of this work has been confined to describing the conditions under which *Anabaena* blooms occur under different flow regimes in the Murray, Murrumbidgee and Darling Rivers (Sherman et al., 1998).

Toxic blooms of *Nodularia spumigena* have occurred in several Australian estuaries or slightly saline lakes (e.g. Peel–Harvey Estuary (WA, Robson, 2000), Lake Alexandrina (SA, Heresztyn and Nicholson, 1997) and Orielton Lagoon (Tasmania)). In the case of the Peel–Harvey Estuary, the 'Dawesville Cut', an artificial channel to increase oceanic flushing of the estuary, was implemented to alleviate severe eutrophication and ecological degradation resulting from *Nodularia* blooms. In summary, neglecting N fixation in inland waters where there are heterocystous cyanobacteria or in coastal regions where *Trichodesmium* is present, can result in poor estimates of N fluxes.

Accurate estimation of N inputs from N-fixation into waterbodies relies upon predicting the presence of N-fixing cyanobacteria and whether or not they are actually fixing N. There is a substantial amount of literature on modelling various aspects of cyanobacterial ecophysiology, including an entire issue of the journal *Hydrobiologia* (Vol. 349, 1997). However, few researchers have attempted to predict the spatial and temporal distributions of cyanobacterial biomass in an environmental setting, let alone the occurrence of N fixation. To further complicate matters, there appear to be a number of environmental triggers to N fixation, aside from ambient N levels, that have not as yet been well resolved. For example, in the Darling–Barwon River system, Donnelly et al. (1997) indicated that iron limitation (or potentially other trace elements, eg. Mo) may have been released at discrete times when there were blooms of N-fixing *Anabaena.* Further, modelling of akinete-forming cyanobacteria such as *Nodularia spumigena* would necessitate at least a simple life cycle representation to capture the very dynamic temporal variations in biomass which are generally associated with changes in salinity (Robson, 2000).

Simple models of N-fixation are given by Gargas (1976) and Levine and Lewis (1987). The model of Levine and Lewis was applied to Lake Valencia in Venezuela to estimate the importance of N-fixation to loading to the lake. The model is based on the number of heterocysts, rather than the biomass of N-fixing cyanobacteria, but it at least provides a preliminary quantitative approach to how to model N fixation. The amount of N fixed per heterocyst is given as:

$$\frac{\partial N}{\partial t} = N_s(1 - e^{-a})e^{-b} + D \qquad (5)$$

where $a = \alpha I N_s^{-1}$ and $b = \beta I N_s^{-1}$ and, on a per heterocyst basis, N_s is the maximum rate of N-fixation in the absence of high light intensities, D is the rate of N-fixation in the dark, I is the light intensity, α is a parameter for the slope of the rising limb of the light response curve and β is a photoinhibition parameter. The major challenge in predicting N-fixation is to link equation 6 to a model of the major environmental factors that trigger the growth of cyanobacteria that can fix N, while also taking into consideration the factors that trigger the switch to N-fixation.

Nitrification

Nitrification is a two-step process involving oxidation of ammonium to nitrite followed by nitrite to nitrate by bacteria of the genus *Nitrosomonas* and *Nitrobacter*, respectively. Recent studies by Hovanec and Delong (1996) and Hovanec et al. (1998) using gel electrophoresis and rDNA libraries, however, have indicated that *Nitrospira* is also important in nitrite oxidation, and *Nitrosomonas* is just one of several bacterial genera that are responsible for ammonium oxidation.

The approach adopted in modelling nitrification has generally been to ignore the intermediate nitrite species so that one nitrification rate constant can be applied across the two transformations. In modelling nitrification there is a fundamental difference in the literature between applications to wastewater treatment systems and applications to natural systems. The equations for wastewater treatment include a biomass for nitrifiers (X_N) as follows:

$$\begin{aligned} \frac{\partial NO}{\partial t} &= \mu_N \frac{NH}{K_N + NH} \frac{DO}{K_{DO} + DO} \frac{X_N}{Y_N} - d_N \frac{X_N}{Y_N} \\ \frac{\partial NH}{\partial t} &= -\mu_N \frac{NH}{K_N + NH} \frac{DO}{K_{DO} + DO} \frac{X_N}{Y_N} + d_N \frac{X_N}{Y_N} \end{aligned} \qquad (6)$$

whereas those for most environmental modelling applications do not explicitly incorporate the bacterial biomass:

$$\begin{aligned} \frac{\partial NO}{\partial t} &= \mu \frac{DO}{K_{DO} + DO} NH \\ \frac{\partial NH}{\partial t} &= -\mu \frac{DO}{K_{DO} + DO} NH \end{aligned} \qquad (7)$$

In equations 6 and 7, μ_N and d_N are the temperature-dependent maximum rates of growth and loss of nitrifiers, K_N and K_{DO} are half saturation constants for ammonium and dissolved oxygen (DO), Y_N is the mass of nitrifying bacteria generated per unit mass of ammonium utilised, and μ is a temperature-dependent rate constant for nitrification. The differences between equations 6 and 7 are not trivial because in environmental modelling applications the first-order dependence on ammonium concentrations is equivalent to assigning ammonium as an analogue for the biomass of nitrifying bacteria. Whereas in equation 6, μ_N represents the actual growth rate of nitrifiers, μ in equation 7 represents a somewhat abstract value that cannot be easily validated across different systems. In ideal circumstances it would be a substantial improvement in natural systems to isolate nitrifying bacteria and determine their biomass so that equation 6 might be applied.

There is a similar divergence of equations between the wastewater and environmental modelling literature for representations of denitrification and ammonification. Wastewater applications generally explicitly represent the biomass of the bacterial group responsible for the transformation and use a Michaelis-Menton dependence on nitrate and organic nitrogen for denitrification and ammonification, respectively. By contrast, most applications to natural aquatic systems use a process rate based on a first-order dependence on the relevant substrate, ie. nitrate or ammonium.

Denitrification

Denitrification refers to the two consecutive reductions of NO_3 to NO_2 and then to N_2 and other gaseous products such as N_2O and NO. This process is carried out by a large number of facultatively aerobic, heterotrophic bacteria. Under aerobic conditions these organisms use oxygen to oxidise organic material but under anoxic conditions they use NO_3 as the electron acceptor. Anaerobic metabolism does not yield the same energy as aerobic metabolism and denitrification should theoretically not occur in the presence of free dissolved oxygen. Nevertheless, it appears to occur in various oxic environments, probably as a result of the existence of anoxic micro-environments associated with particle biofilms (Paerl and Pinckney, 1996). Therefore, models of denitrification generally include an inverse dependence on dissolved oxygen to represent reduced rates associated with increasing diffusion of dissolved oxygen into anoxic microenvironments.

It seems reasonable that if the microenvironment hypothesis is valid then also the presence of particulates, aggregates or biofilms that may serve as hosts for such processes should also be included in formulating equations for denitrification. This presents a major difficulty from a modelling perspective since relevant variables such as NO_3 and DO are actually measured in the bulk water and not within particle microenvironments or in the sediments or sediment-water boundary layer. Neglecting this fact, a general form of the equation for denitrification can be written as:

$$\frac{\partial NO}{\partial t} = -\mu \frac{K_{DN}}{K_{DN} + DO} NO \qquad (8)$$

where μ is the temperature dependent rate constant for denitrification and K_{DN} is the inverted half saturation constant for the effect of dissolved oxygen concentrations on denitrification. Several other factors besides dissolved oxygen and temperature can affect rates of denitrification, including pH and availability of labile organic carbon. Kadlec and Knight (1993), for example, include a Michaelis-Menton formulation for dissolved organic carbon (DOC) on the right hand side of equation 8 and give a half saturation constant for DOC of 0.1 mg/L.

Most of the published information on rates of denitrification in Australia has arisen from the Port Phillip Bay study conducted in the early 1990s. Denitrification efficiencies for N processed in the sediments were 75–85% but declined close to zero as organic C: N ratios increased well above the Redfield ratio (Heggie et al., 1999). In developing a model of denitrification for Port Phillip Bay, Victoria, Murray and Parslow (1997) incorporated state variables of microphytobenthos, seagrass, macro-algae and benthic filter feeders to more accurately quantify rates of denitrification associated with cycling of nitrogen, carbon and dissolved oxygen through the sediments. In most shallow coastal and estuarine systems, denitrification generally accounts for greater than 50% of the nitrogen lost, and macrophytic epibenthos plays a key role in providing biofilm surfaces and diurnal cycling of dissolved oxygen and redox within the sediments. Diurnal cycling will be captured only by models that operate at sub-daily time steps, otherwise measurements of denitrification rates, using benthic chambers for example, will not be useful for setting model parameter values.

A requirement to model benthic primary production is inescapable for sediments in the euphotic zone if major nitrogen fluxes are to be captured, to estimate not only assimilation of nutrients by primary producers, but also their indirect role in denitrification. The above discussion also applies to shallow lakes, where denitrification rates are generally not as high as in estuaries and coastal seas, but where the littoral zone and macrophytes nevertheless play an important role in removing available N.

Other considerations

In this paper I do not deal with nitrogen uptake by primary producers, cycling of nitrogen through the food chain or ammonification. There are many models that include N assimilation by planktonic and benthic producers, and the major difference between these models is whether a fixed internal nutrient ratio of C: N: P is used (approximating to the Redfield ratio) or whether luxury uptake is included. The former case considers that growth is influenced directly by ambient nutrient concentrations whereas the luxury uptake case operates independently model for growth and uptake. There are also several models that include various levels of complexity to differentiate between uptake of nitrate and ammonium by primary producers (eg. Flynn et al., 1997). The main variation in environmental models of ammonification is whether or not effects of dissolved oxygen are included. A review of the literature indicates that rates of ammonification under anoxic conditions can be anywhere from 40% to over 90% of those under oxic conditions. The relative contributions of labile and refractory N and the ratio of macronutrients in the organic matter probably play important roles in determining the influence of dissolved oxygen on ammonification rates, but have not yet been addressed.

The development of improved process representations and greater predictive accuracy of numerical models will be dependent on supplementing recent improvements in our conceptual understanding of N dynamics with measurements and sensitivity analysis of the various N fluxes. The time and space scales at which numerical models operate will also be critical and need to be addressed so that field and laboratory validation measurements are directly applicable to the fluxes represented in models.

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Modelling denitrification in aquatic sediments

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Introduction

This paper shows how denitrification might be modelled in aquatic sediments. In particular, the paper addresses how denitrification can be represented in a depth-resolved diagenesis model, diagenesis being the process of organic matter degradation in sediments. There have been a number of diagenesis models which represent the stratigraphy of sediments, including CANDI (Boudreau, 1996) and STEADYSEDI (Van Capellan and Wang, 1996). In the following analysis, I choose the Blackburn and Blackburn (BB) model (Blackburn and Blackburn, 1993) to represent diagenesis. It lacks many of the species incorporated in other models (P, Fe, Mn), but it has the most sophisticated and realistic representation of the elementary processes producing particulate organic matter, dissolved organic matter and nitrate.

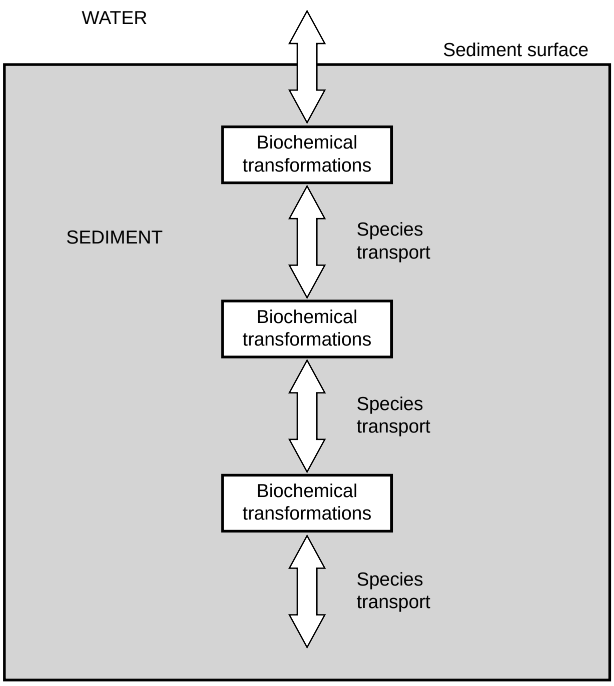

Figure 1. Schematic of model structure

The BB model

The BB model simulates C–N–S–O cycling within marine sediments. This model slices the sediment into a series of vertically stacked layers in which biochemical transformations occur according to species concentrations within the layers (Figure 1). Exchange of chemical species occurs between adjacent layers.

Biochemical reactions

The model is fuelled by the oxidation of detrital matter settling onto the sediment surface and mixed downwards into the sediment. This detrital matter is represented in the model as particulate organic carbon (POC) and as particulate organic nitrogen (PON). The POC and PON are made available for reaction after they have been hydrolysed to dissolved organic carbon (DOC) and dissolved organic nitrogen (DON). The model reactions are:

$$POC \rightarrow DOC \qquad \text{hydrolysis}$$

$$DOC + O_2 \rightarrow CO_2$$

$$2\ DOC + SO_4 \rightarrow 2\ CO_2 + HS$$

$$1.25\ DOC + NO_3 \rightarrow 1.25\ CO_2 + 0.5\ N_2 \qquad \text{denitrification}$$

$$PON \rightarrow DON \qquad \text{hydrolysis}$$

$$DON \rightarrow NH_4$$

$$NH_4 + 2\ O_2 \rightarrow NO_3 \qquad \text{nitrification}$$

$$HS + 2\ O_2 \rightarrow SO_4$$

The DOC is oxidised by O_2, NO_3, or SO_4, depending on the concentrations of these species within a particular layer. DON is converted to NH_4; NH_4 and HS are oxidised by O_2. The reduction of NO_3 by DOC is denitrification, which releases N_2 gas.

The above reactions are represented using simple mathematical relationships. For example, the hydrolysis of DOC to POC is represented by:

$$\frac{\partial\, DOC}{\partial\, t} = k_{DOC}\ POC$$

where DOC and POC are concentrations, t is time, and k_{DOC} is a hydrolysis rate constant. The representation of the denitrification rate is illustrative of the rates of reaction which depend on the concentrations of other species:

$$\frac{\partial\, N_{N2}}{\partial\, t} = k_{N2}\ \alpha_{NO3}\ \beta_{O2}\ DOC$$

Here k_{N2} is a rate constant, α_{NO3} is a stimulation factor whose value increases linearly to a maximum value of unity with increasing nitrate concentration, and β_{O2} is an inhibition factor which starts at unity for low values of oxygen concentration and which decreases linearly to zero at higher values.

The stimulation and inhibition factors are representations of the responses of aerobes and anaerobic bacteria, respectively. Nitrification requires oxygen, whereas denitrification requires an anoxic environment. The conversion of ammonia to nitrogen gas is most efficient when an oxic and anoxic zone are close to one another. Real sediments have a considerable degree of heterogeneity not represented in the smoothed (by diffusion) one-dimensional model structure. The distribution of organic matter around individual sediment grains is likely to create strong variations in oxygen demand and oxygen concentrations on sub-millimetre length scales. Reactions which might be expected not to occur together in a particular depth layer or at a given mean-layer oxygen concentration may co-occur in reality (Harris et al., 1996). The model accounts for this by implementing ramping stimulation and inhibition functions which allow nitrification and denitrification to proceed at the same depth. The range of oxygen concentration over which ramping is implemented profoundly affects model performance. In the present BB model implementation, stimulation reaches unity and the inhibition declines to zero at an oxygen concentration of 30 μM.

Species transport

In the BB model, species transport between adjacent sediment layers occurs mostly by molecular diffusion. The diffusivity varies with the chemical species, sediment tortuosity, and temperature. For POC and PON, transport is also assumed to be a diffusive process, but in reality particulate transport must occur via other processes such as bioturbation. Species transport can be readily modified to account for other non-diffusive processes such as pumping by organisms or by other physical phenomena such as waves. Sometimes such bio-activity can be represented by enhanced diffusivity coefficients, but other times bio-activity leads to transport which is fundamentally different from diffusion-type processes. An example of such transport is non-local advection which occurs when deposit feeders excrete at depth within the sediment effectively by-passing the intermediate sediment layer (Boudreau, 1996). How fast dissolved and solid-phase species are transported is critically important for model performance.

Model solution

The system of coupled reaction and transport equations is solved numerically by a finite difference procedure. A set of reaction coefficients and diffusivities is prescribed. Figure 2a shows profiles of O_2, NO_3, and SO_4 predicted using a sample run of the model. Oxygen diffuses down from the sediment surface and is depleted as it is consumed in the oxidation of DOC, NO_3, and HS. Oxygen concentrations go to near zero a few millimetres below the sediment surface which is not dissimilar to what occurs in many aquatic sediments, including Port Phillip Bay. Nitrate is maximal at about 0.5 cm depth around where it is produced by the oxidation of NH_4. The background level of SO_4 is that of seawater. At depth, its concentration is reduced where it contributes to the oxidation of DOC.

The predicted relative contributions of the oxidants of DOC (O_2, NO_3, SO_4) are shown in Figure 2b. In the oxic zone near the sediment surface, O_2 is the major oxidant, but in the deeper anoxic zone SO_4 is the major oxidant. The oxidation by NO_3 (denitrification) is largest near the oxic–anoxic boundary. Note that what is modelled is a marine sediment; sulfate would generally not be so readily available as an oxidant in freshwater sediments. More sophisticated models would allow for other oxidising agents including Fe and Mn.

Denitrification

Denitrification is a key mechanism for stripping nitrogen from aquatic systems, but its role in the biochemical function of lakes, rivers, and estuaries depends very much on the interaction with many other processes in the water column and sediments, including primary production and bacterial degradation. In biogeochemical models of aquatic systems, (sediment) denitrification is a process which responds to the flux of organic detritus to the sediment surface.

Figure 3 shows the predicted denitrification efficiency as a function of the respiration rate of the sediment expressed as the equivalent flux of nitrogen. Efficiency is defined as the ratio of the areal denitrification rate to the PON flux from the water column. These model predictions assumed the set of parameters suggested by

Blackburn and Blackburn (1993). The rate constant for POC and PON hydrolysis in the base simulations (k_1) was set to 0.01 d^{-1}. In effect, this rate determines the degradation rate of the organic matter. The assumed C:N ratio for the organic matter is seven.

At low loading rates, the denitrification efficiency is close to zero. The ammonia produced through degradation is oxidised to nitrate, but there is insufficient DOC remaining to react with the nitrate and hence there is little denitrification. The denitrification efficiency increases to a maximum of 34% at a respiration rate of 18 mg-N $m^{-2}d^{-1}$. At higher loads the denitrification efficiency declines as the relative amount of oxygen available for the nitrification step declines. The efficiency of denitrification depends on other factors including species transport rates and reactivity. Also shown in Figure 3 are denitrification efficiencies calculated for k_1 = 0.05 d^{-1}. Maximum efficiency in this case reduces to 23%. Murray and Parslow (1997) suggest that simple diffusion models should have a maximum denitrification efficiency of 50% if the nitrate is produced within the sediment.

Measured denitrification efficiencies have been well above 50%. Efficiencies measured in Port Phillip Bay using benthic chambers were mostly above 50% (Murray and Parslow 1997) although it is suggested that these efficiencies were calculated on gross respiration and should be calculated on net respiration which includes microphytobenthic photosynthesis. It is not clear how big the correction should be, but maximum efficiencies were calculated at the centre of Port Phillip Bay where microphytobenthic production was generally low. Murray and Parslow used an empirical expression for denitrification in their ecological model of the bay and this is shown also in Figure 3. Their assumed maximum efficiency of 70% occurs at a respiration rate of 10 mmol $m^{-2}d^{-1}$ and is about double the maximum efficiency indicated from simulations using the BB model.

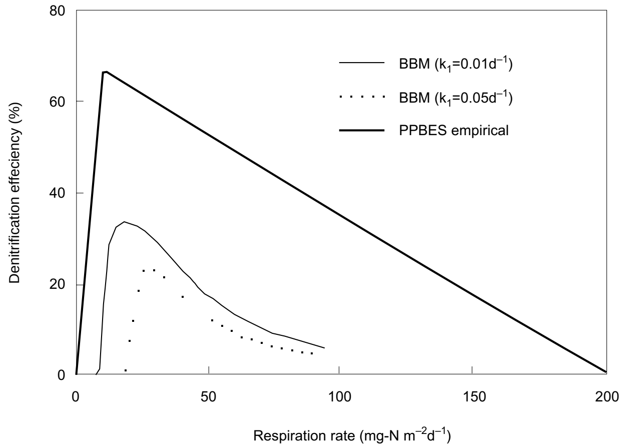

Figure 3. Modelled denitrification efficiency versus sediment respiration computed from the BB model for two values of the hydrolysis rate. Also shown is the empirical form used by Murray and Parslow (1997) for Port Phillip Bay.

Microphytobenthos

Murray and Parslow (1997) postulate that microphytobenthos (MPB) could have a major impact on net effective denitrification rates within the sediments of Port Phillip Bay. In their 'facilitative' model, they suggest that MPB enhances effective denitrification efficiency by trapping dissolved inorganic nitrogen (nitrate + ammonia) which would otherwise escape from the sediment. The MPB biomass is eventually converted into decomposing organic matter which re-enters the denitrification loop. Consequently, the effective PON flux driving

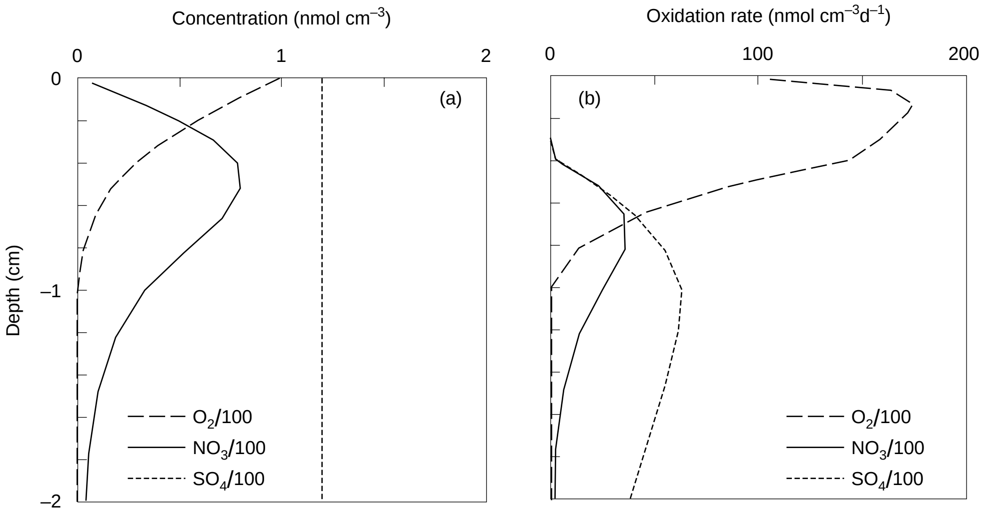

Figure 2. (a) Concentration profiles of O_2, NO_3 and SO_4; (b) Rates of oxidation of DOC by O_2, NO_3 and SO_4

denitrification is not just that arriving from the water column, but it should also include a component deriving from the decomposition of MPB at the sediment surface.

In Lake Illawarra, a coastal lagoon, measured benthic primary production was five times that of the water column. Suppose the net PON flux from the water column was 2 mmol $m^{-2}d^{-1}$, which is approximately the measured level of primary production for the lake, and suppose the net PON flux from the MPB layer into the sediments below was five times this, namely 10 mmol $m^{-2}d^{-1}$. For the modelled case of $k_1 = 0.05\ d^{-1}$, the efficiency of denitrification at a PON flux of 10 mmol $m^{-2}d^{-1}$ (modelled sediment respiration rate approx. 60 mg-N $m^{-2}d^{-1}$) is 9% giving a denitrification rate of 0.9 mmol $m^{-2}d^{-1}$. However, the efficiency of denitrification calculated in terms of the net PON flux from the water column is 0.9/2 or 45%, which is double the 23% efficiency at the assumed water column PON flux of 2 mmol $m^{-2}d^{-1}$ (modelled sediment respiration rate approx. 14 mg–N $m^{-2}d^{-1}$).

This analysis assumes that the MPB occurs as a very thin layer on the sediment surface, but it is known to spread itself through the top millimetres of sediments; that is, through the zones of nitrification and denitrification. Further, MPB produces oxygen during the day and at night oxygen is consumed through respiration. This behaviour would be expected to cause the boundary between the oxic and anoxic zones to cycle up and down on a diurnal basis, a phenomenon not accounted for in the BB model as implemented. Using microelectrodes, Lorenzen et al. (1998) showed that such a translocation of this boundary occurs in freshwater cores subject to light and dark conditions. Lorenzen et al. inferred profiles of denitrification rate based on an analysis of measured nitrate and oxygen microprofiles. The denitrification zones also migrated vertically in response to the light conditions (Figure 4).

In order to increase our understanding of how MPB impacts the denitrification process, Z. Wang (a PhD student at CSIRO Land and Water in Canberra) is undertaking a modelling study of sediment diagenesis which includes the MPB. The model is closely based on the CANDI model, which is essentially similar to the BB model. So far, the results are encouraging. Wang has managed to model the oxygen, nitrate, and denitrification profiles as they respond to light and dark reasonably well. The depths of the denitrification zones are well modelled, although the magnitudes of the rates are simulated within a factor of two (Figure 4). The magnitude simulation can certainly be improved by assuming an organic matter degradation rate that decreases with depth within the sediment. The analysis of the model results and their implications are currently under way.

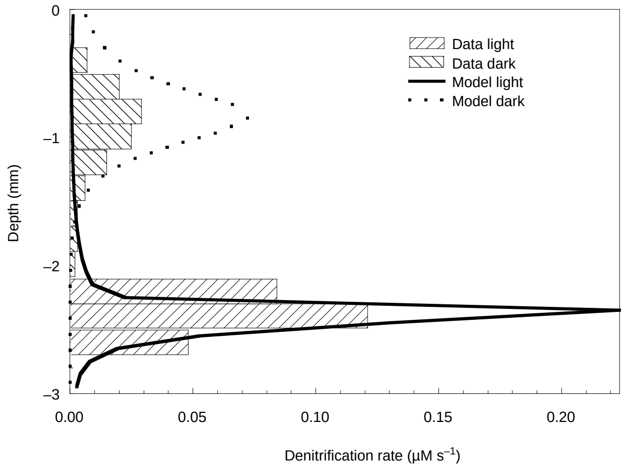

Figure 4 Denitrification rates measured by Lorenzen et. al. (1998) in light and dark cores. These are compared to model simulations by Z. Wang.

Conclusions

In this paper, I have addressed the issue of how denitrification in sediments might be modelled. At the present time, it seems that the success of modelling is somewhat equivocal. Good reasons for this situation include the neglect of important processes such as the influence of microphytobenthos. A study is currently under way which addresses this particular omission. Further deficiencies include adequate representation of the effects of other bio-activity. The respiratory, burrowing, feeding, and excretory behaviour of benthic organisms moves dissolved and solid matter vertically through the sediment column and is certain to have a first-order impact on sediment biogeochemistry and denitrification rates. Biota are capable also of producing heterogeneity within sediments which is likely to enhance denitrification. Burrows of organisms such as worms and shrimp represent an increased benthic surface area over which denitrification can occur.

Ultimately, even if diagenesis models are capable of including all of the biotic effects, their application will likely remain site specific and require supporting studies. The principal values of modelling will be in the diagnosis of sediment processes and in the development of ‘what if?’ scenarios. Used in diagnostic mode, models are an important tool for unravelling the intricacies of complex interacting processes which affect denitrification. Used in ‘what if?’ mode, models can assess the likely impact of management actions on denitrification. For example, what would be the impact of altering the population of MPB through increased turbidity?

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The influence of inorganic nitrogen and its various forms on the growth and species composition of phytoplankton communities

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Introduction

A great deal of research has been carried out, and much continues to be done, in an effort to identify nutrient limitation of phytoplankton growth in both marine and freshwater systems. There are several reasons for the prolonged and intensive research on this issue and for the passionate debates that rage around the identification of nutrient limitation. Foremost is the importance of understanding the role of nutrients in controlling phytoplankton growth so that the biomass production and the species composition of phytoplankton communities can be managed. This is of major importance in freshwaters where potable, agricultural and industrial supplies are put at risk by growth of problem species of phytoplankton. Just as important, however, is the need to manage phytoplankton and micro-algal populations to ensure the continued support of aquatic food webs that maintain the water quality and productivity of inland waters. In marine systems, an understanding of nutrient influences on phytoplankton is similarly important for managing toxic blooms impacting on estuarine and coastal fisheries. But equally important is an understanding of nutrient impacts on total oceanic productivity, not only for maintaining harvestable stocks of fishes but also for modelling fluxes of major gases that affect global warming and buffer climatic fluctuations. The importance of making the correct decisions with regard to nutrient management, especially on a global scale, coupled with the difficulties of making reliable and unequivocal measurements that identify a specific nutrient limitation, drives the continuing debate.

Phytoplankton growth is influenced by many environmental factors, but when light and temperature are adequate and cell loss rates are low, then the phytoplankton biomass increases to an extent governed by the nutrient supply. As the phytoplankton biomass increases, a larger proportion of the dissolved nutrients available to support growth is incorporated into the phytoplankton cells leaving less in solution for assimilation. If there is no re-supply of available nutrients, then the phytoplankton biomass can continue to increase only until the nutrient in shortest supply, the yield limiting nutrient, is exhausted. At this point the phytoplankton biomass is maximal and further growth is restrained by the depleted nutrient. If the biomass yield per unit of limiting nutrient is known, then the maximum potential phytoplankton biomass can be predicted from a measurement of the available quantity of the limiting nutrient.

In many aquatic systems this simple picture is complicated by nutrient re-supply that occurs either from internal sources such as suspended particles and the bottom sediments, or from external sources including inflows from the catchment or supply from the atmosphere. Nutrient re-supply complicates the task of identifying nutrient limitation of phytoplankton since measurements of immediately available nutrient concentrations do not represent the total nutrient available to support phytoplankton growth. Consequently, a low nutrient concentration does not indicate nutrient limitation, as re-supply could be occurring at a rate matched by nutrient uptake by the phytoplankton. Even if the concentration is sufficiently low as to restrict the *rate* of phytoplankton growth (rate limiting nutrient) it will not necessarily regulate the phytoplankton biomass that develops (yield limiting nutrient). The significant point of this scenario is that it is possible for one nutrient to limit the growth rate of phytoplankton because it is at a low concentration but for a second nutrient to limit biomass yield because it is in shortest supply and exhausted first. These subtleties are important in understanding and interpreting data on nutrient limitation of phytoplankton growth and are relevant to the following discussion on how nitrogen (N) supply impacts on phytoplankton communities.

The issue of nutrient re-supply highlights a fundamental difference between the phosphorus (P) and N cycles in aquatic systems. Nitrogen, unlike P, has a gaseous form and can readily exchange with the atmosphere. Whereas the re-supply of P is largely restricted to inflows from the catchment and nutrient recycling from the bottom sediments, N can additionally be supplied from the atmosphere as dissolved N gas. Although the majority of phytoplankton cannot use this form of N it can be assimilated by specialised, N-fixing species of cyanobacteria. The connection between the N cycle and the atmosphere also allows for N to be lost from the system as N gas, so reducing the total N content. An important consequence of this difference in the nutrient cycles is that the relative quantities of N and P available to support phytoplankton growth are not solely dependent on loads from the catchment but can be modified by conditions that alter the exchange of N with the atmosphere.

Nitrogen and P are the nutrients most frequently identified as being in limiting supply in aquatic systems (Hecky and Kilham, 1988). On average, phytoplankton growth uses N and P in the mole ratio of 16:1 or 7:1 by weight. This ratio can be used to identify which of these nutrients is in limiting supply from analyses of nutrient concentrations, provided that the total supply of available nutrient is measured and that phytoplankton growth reduces one of the nutrients to limiting levels. The exchange of N with the atmosphere can lead to significant shifts in this ratio and so to changes in the limiting nutrient. The presence or absence of a N deficit relative to the P supply has major repercussions for the nutrient status of aquatic systems, for nutrient limitation of phytoplankton and for the success of specific phytoplankton species. It is these interactions that are highlighted in the following sections.

Nutrients and phytoplankton biomass

As noted above, nitrogen and P are the nutrients most frequently identified as being in limiting supply and responsible for regulating the biomass of phytoplankton both in freshwater and marine systems. The paradigm has developed that freshwaters are P limited and marine systems N limited but these generalisations must be treated cautiously, as they are not always reliable. Indeed, if recent models of phytoplankton production in the global ocean are substantiated then P is the major nutrient controlling long-term changes in biomass of the marine phytoplankton while N limitation controls the immediate biomass levels (Tyrrell, 1999).

In freshwater systems there is a large body of data, especially for temperate lakes, that demonstrates a strong correlation between P supply and the maximum phytoplankton biomass (Vollenweider,1968). It is from these relationships that the major role of P in regulating phytoplankton biomass has been derived. However, it cannot be concluded from these relationships that P is always the nutrient in shortest supply and, in fact, in many freshwater systems, N has been identified as the nutrient that is initially limiting to phytoplankton growth (Elser et al., 1990). Similar results have been obtained in Australian systems, where physiological assays and bioassays have demonstrated that N is initially limiting in a range of inland waters (Wood and Oliver, 1995). However, even when N is initially in limiting supply, the final phytoplankton biomass is still often controlled by the availability of P (Howarth et al., 1988). The reason for this is that the N deficit stimulates the growth of N-fixing phytoplankton, all of which are species of cyanobacteria, and these organisms grow using dissolved gaseous N until a second nutrient limitation occurs. In most cases the next nutrient to limit growth is P.

Nitrogen fixation is energetically expensive and provides an advantage only when dissolved inorganic sources of N are at low concentrations. It has been estimated that, for N fixation to occur, dissolved inorganic N concentrations need to be less than 50–100 µg N/L (Horne and Commins, 1987). Critical concentrations of this type are very useful for assessing the likely outcome of particular nutrient conditions but they require further testing. In most cases this type of information is unavailable for Australian waters.

In some aquatic systems where environmental conditions are not conducive to the growth of N-fixing cyanobacteria, N deficits are not fully compensated for by N fixation (Howarth et al., 1988). In these systems, N remains limiting and the maximum phytoplankton biomass is regulated by the N supply. Similarly, N deficits are not always compensated for in lakes that have nutrient inputs with extremely low N:P ratios, or where denitrification has resulted in extremely low ratios. In these situations it appears that the period suitable for N-fixing cyanobacteria to grow and for N fixation to occur is often not sufficiently long to enable the deficit to be removed even though N fixers are present. In these situations it is unlikely that the N fixers are N limited but other phytoplankton species will be.

Nutrients and phytoplankton community composition

The relative availability of different nutrients can influence the species composition of the phytoplankton community. A clear example of this is the advantage that N fixing cyanobacteria have when N:P ratios are low and concentrations of combined inorganic N are reduced to limiting levels by algal growth (Oliver and Ganf, 1999). Correlation analyses of the relationship between the occurrence of cyanobacteria and N:P ratios indicate that cyanobacteria are more likely to occur when N:P ratios are reduced. Conversely, when N:P ratios are high cyanobacteria are less likely to appear (Smith, 1983).

In addition to changes in community composition brought about by shifts in the availability of different nutrients, community composition may also change if different chemical forms of a particular nutrient favour different phytoplankton species (Blomqvist et al., 1994). This occurs if there are species differences in the uptake and assimilation of different chemical forms of a particular nutrient. Phosphorus has only one form that is available for uptake by phytoplankton whereas N occurs in several inorganic forms that can be assimilated. The major forms of N available for uptake by the phytoplankton are nitrate and ammonium, and also dissolved N gas in the case of N-fixing cyanobacteria.

It is evident that the N-fixing cyanobacteria are advantaged when combined inorganic N concentrations are low. In an effort to explain the occurrence of other cyanobacteria, Blomqvist et al. (1994) suggested that non-nitrogen fixing cyanobacteria are favoured by ammonium, while eukaryotic micro-algae are favoured by nitrate. From a review of the physiological data, Oliver and Ganf (1999) concluded that ammonium was a suitable source of N for all phytoplankton but that the non-nitrogen fixing cyanobacteria like *Microcystis* seemed to be disadvantaged when using nitrate under sub-optimal light conditions. There are insufficient data to confirm these interactions and even less information on the occurrence of these processes in nature, but if substantiated they have important implications for management of phytoplankton populations.

Recent studies on marine micro-algae have indicated that other groups of phytoplankton may also require particular forms of N under certain circumstances. Diatom growth is often confined to conditions of high nitrate, low temperature and high turbulent mixing. Under these conditions, cells can accumulate significant amounts of nitrate that is not incorporated into cell material (Lomas and Glibert, 1999). It has been suggested that the nitrate acts as a sink for excess energy capture by the cells as they are mixed close to the surface where high light intensities greatly exceed the mean intensities that they are adapted to. If nitrate is not available then cell growth may be restricted. Much more information of this type is required on the specific N requirements of particular phytoplankton groups, especially if N conditions are to be modified for the purposes of managing phytoplankton growth.

Nutrient storage enables cells to survive transient periods of nutrient depletion and to maintain growth rates when nutrient supplies are spatially or temporally separated. Cyanobacteria is the only group amongst the phytoplankton with a specific N storage compound, cyanophycin, a co-polymer of two amino acids, arginine and aspartate. Presumably this provides some advantage to these organisms, although this has not been clearly demonstrated. Other phytoplankton can increase internal cell concentrations of N that may act as stores over the short term but the importance of this under natural conditions is unknown.

Interactions of cycles and phytoplankton growth

To some extent it could be argued that P supply most often regulates the maximum phytoplankton biomass but that N in its various forms has a substantial influence on population dynamics and community structure. Consequently, modification of the N status of waters could be used to alter the composition of the phytoplankton community.

Removal of N to the atmosphere is the result of denitrification, the transformation of nitrate to N gas. Nitrate is supplied from the catchment or it can be produced by nitrification of ammonia that forms from the breakdown of organic material. These transformations depend on a number of conditions including the oxygen and redox status of both the sediments and the lower water column, the organic carbon supply and also the temperature. Consequently, by manipulating these conditions there are opportunities to manage the N content and the forms of inorganic N that are present within an aquatic system and through these manipulations to influence the phytoplankton community structure and even its biomass. Relatively simple modelling procedures based on the sediment oxygen content have been used to predict N transformations and preliminary criteria have been derived that can help with setting management targets (Murray and Parslow, 1999). For example, it has been proposed that oxygen concentrations of less than 0.2 mg/L are required for denitrification to occur. However, the interactions between these transformations require further definition if they are to become useful management tools.

The Australian perspective

Very little information is available on the N cycle in Australian freshwaters. Most of the monitoring effort has been aimed at evaluating the nutrient status of surface waters from measurements of nutrient concentrations. This information provides essential background to identifying the extent of eutrophication but provides little insight to nutrient dynamics. In addition, much of the analysis has been focused on P and its link with phytoplankton biomass production. In some cases N measurements have been made and these data warrant further analysis.

More recently it has been demonstrated using bioassays and physiological assays that N limitation occurs in a range of inland systems and that this may be responsible for the widespread occurrence of N-fixing cyanobacteria, particularly in the regulated river systems (Wood and

Oliver, 1995). However, there are few detailed measurements of the nutrient conditions that fostered the development of these organisms and it is unclear whether a N deficit occurs because there are low inputs of N from the catchment or because denitrification removes nitrate from the system.

Despite the widespread and problematic occurrence of N-fixing cyanobacteria very little is known about their nutritional status. As N limitation seems a likely precursor to their development it is presumed that N fixation is occurring, but direct measurements of N fixation rates could not be found. Consequently, we have no information on the extent of N fixation or whether it is modified or restricted by the supply of trace metals and other co-factors required as part of the metabolic process. The importance of this source of N to aquatic food-chains is also unknown.

The effects of changes in the form of N on phytoplankton community composition and the growth of particular species appears not to have been studied in detail for any Australian inland system. This is an area that requires major investigation using both field and laboratory studies. There is also a need to link this with measurements of the aquatic N cycle to provide an integrated understanding of these interactions.

The need for this information is critical because there are potential dangers in manipulating nutrient supplies to waterways without a clear understanding of their consequences. Increasing nutrient pressures on waterways require management decisions to control the nutrient loads but this assumes some knowledge of the interactions within the system. Currently our understanding of these interactions is sketchy.

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The importance of benthic micro-algae, in the context of nitrogen biogeochemistry, to Australian freshwater systems

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Abstract

Benthic micro-algae are quantitatively important components of marine and freshwater ecosystems. This paper discusses the significance of benthic micro-algae in terms of direct nitrogen (N) uptake and various bacterial transformations mediated by photosynthetic O_2 production. Although much of our current understanding of the role of benthic micro-algae in the biogeochemical cycling of N is based on marine environments, the processes presented here are equally relevant to freshwater ecosystems. Gaps in our understanding of the significance of benthic micro-algal mediated N transformations and fluxes are also discussed.

Introduction

Benthic micro-algae, sometimes referred to as microphytobenthos, is the functional group of photosynthetic microflora (eukaryotic algae and cyanobacteria) that occurs in association with sediments in a range of aquatic environments. Though usually inconspicuous, benthic micro-algae are often the dominant autotrophic components of coastal habitats ranging from salt marshes to continental shelves. Benthic micro-algae are an equally important component of freshwater environments ranging from standing water bodies to river systems.

While early studies relate mainly to floristics and systematics, recent attention has focused on the role benthic micro-algae play in the energetics and cycling of nutrients in aquatic systems. When particularly abundant, benthic micro-algae excrete mucilaginous films to form a dark, fibrous, consolidated mat over the sediment surface which can reduce the degree of sediment re-suspension in areas of high bottom shear. Increased sediment stability has implications for general water quality in so far nutrient release from suspended sediments is suppressed and a barrier against solute diffusion across the sediment–water interface is formed.

More recent attention has focused on the 'active' role of benthic micro-algae in the biogeochemical cycling of nitrogen. Much of this current understanding is based on international studies undertaken in marine and estuarine ecosystems, with comparatively fewer studies undertaken in freshwater systems. Since the Port Phillip Bay Environmental Study, there has been wider recognition of the potential importance of the role of benthic micro-algae in mediating nitrogen transformations and fluxes in both marine and freshwater environments.

A conceptual model

Our conceptual understanding of N cycling at the sediment–water interface colonised by benthic micro-algae involves the processes of assimilation, mineralisation, nitrification and denitrification (Figure 1).

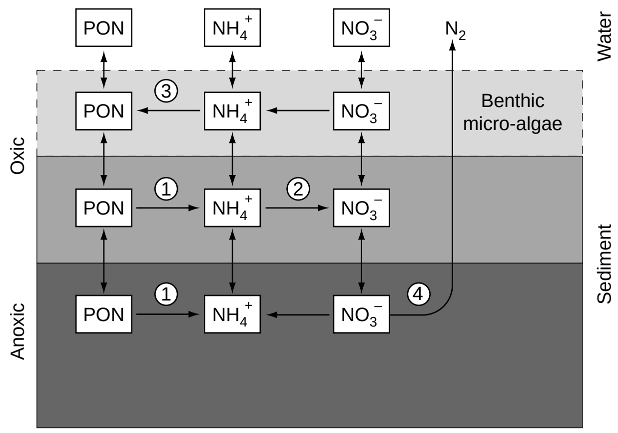

Figure 1. Vertical cross-section of sediment colonised by benthic micro-algae. The sediment is composed of an oxic layer and an anoxic layer. Numbers refer to the processes: 1. mineralisation; 2. nitrification; 3. assimilation; and 4. denitrification. Abstracted from Rysgaard et al. (1993).

As summarised in Figure 1, benthic micro-algae can:

- regulate oxygen conditions (photosynthesis and respiration) at the sediment–water interface where bacterial action mineralises particulate organic N to inorganic forms;

- intercept and assimilate re-mineralised inorganic N at the sediment–water interface;
- increase nitrification rates of NH_4^+ by increasing the sediment oxic depth during photosynthesis; and
- stimulate denitrification through an increased supply of NO_3^- within the sediments.

NO_{3-} and NH_4^+ can also be stripped from the water column and similarly processed. Because benthic micro-algal photosynthesis is driven by light, these N transformations and fluxes occur at temporal scales ranging from diurnal to seasonal.

Benthic micro-algae can play a significant role in N assimilation and nitrification / denitrification in aquatic environments, whether marine or freshwater. The role of benthic micro-algae in these key ecosystem processes is worthy of further discussion.

Benthic micro-algal N assimilation

Located at the site of maximum nutrient regeneration, the sediment–water interface, benthic micro-algae can intercept and assimilate inorganic N from the mineralisation of particulate organic matter. The conversion, or biological fixation, of inorganic N to benthic micro-algal biomass can be an important pathway for N in aquatic ecosystems dominated by benthic micro-algae. The presence of benthic micro-algae has been shown to reduce the efflux of inorganic N from the sediment, with a minimum efflux occurring during periods of increased illumination (Figure 2).

However, directly measured flux data from benthic chambers (light and dark) are difficult to interpret because several, if not all, the processes summarised in Figure 1 occur simultaneously. The capacity of benthic micro-algae to assimilate N during periods of darkness is also often ignored in some studies. A simple alternative method to examine the potential importance of benthic micro-algal assimilation is to estimate the inorganic N requirements of this functional group indirectly from primary productivity data and simple stoichiometric models.

Benthic micro-algae can contribute significantly to total system primary productivity on both a specific locality and global basis. Several studies have also shown that benthic micro-algal primary productivity is comparable to, if not greater than, phytoplankton production on an areal basis. Benthic micro-algae are ubiquitous in systems dominated by soft sediment substrates and have been shown to be extremely low light adapted. Despite both these conditions characterising most freshwater environments, benthic micro-algal primary productivity data for freshwater ecosystems are scant.

We get a better appreciation of the role benthic micro-algae play in N assimilation by looking at the group's inorganic N requirements in relation to the N budget for an entire water body. Within Australia, such an examination was recently undertaken as part of the Port Phillip Bay Environmental Study (Table 1).

Based on biomass (chlorophyll a) and primary production estimates, these data indicate that the dissolved inorganic nitrogen (DIN) requirements of benthic micro-algae in Port Phillip Bay are in the order of 20,000 t y^{-1}. Moreover, the estimated mean turnover rate suggests that

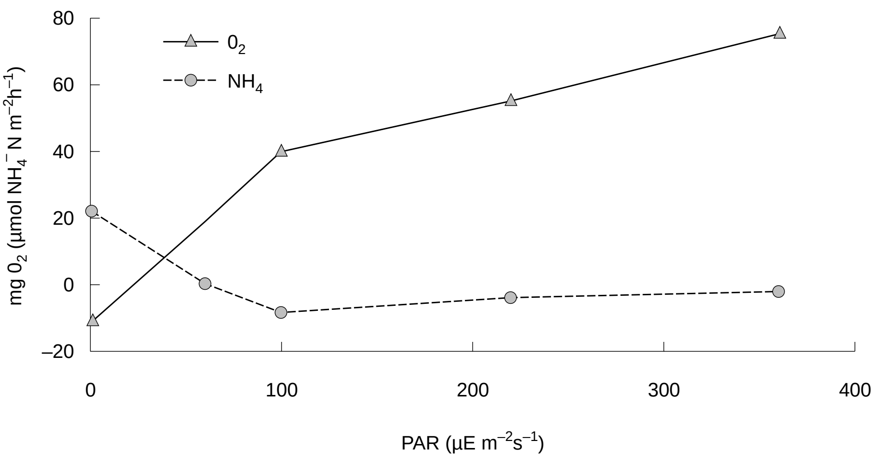

Figure 2. Relationship between O_2 and NH_4^+ fluxes, across the sediment–water interface, as a function of irradiance in a shallow estuarine sediment colonised by benthic micro-algae. Positive fluxes denote release of material from sediments. From Rizzo et al. (1996).

this N pool is cycled back through the sediments approximately 50 times per year. Benthic micro-algal N assimilation represents approximately four times the external loading of DIN to this system and approximately 60% of the total N requirements of the phytoplankton population.

It is estimated that in Port Phillip Bay between 43 and 55% of the DIN regenerated annually from the benthos may be intercepted by benthic micro-algae and used to support high rates of primary production. The assimilation of regenerated nutrient, particularly ammonium, at the sediment–water interface has important implications for general water quality and can limit phytoplankton productivity and the frequency of episodic water column blooms.

Nitrification/denitrification

Biological N fixation at this scale suggests the release of significant quantities of O_2. It has long been thought that benthic micro-algal photosynthetic O_2 production may play a significant role in the biogeochemical cycling of N in aquatic environments. However, early hypotheses were difficult to test. This is an area of research which has received significant recent attention.

The simultaneous nature of assimilation and nitrification/ denitrification processes presented challenges in methodology which have only recently been met by newly developed techniques. Acetylene blocking, isotope pairing, direct N_2 efflux measurement and microsensor techniques all contributed significantly to our understanding of the role of benthic micro-algae in the processes of nitrification and denitrification. However, these techniques often gave rise to ambiguous and sometimes conflicting results.

The advent of micro-scale NO_3^- biosensors has provided the best insight yet into the role that benthic micro-algal photosynthetic O_2 production plays in regulating the processes of nitrification and denitrification (Figure 3). The data plotted in Figure 3 clearly demonstrate a lack of denitrification during darkness whereas high rates of denitrification and a tight coupling between nitrification and denitrification are stimulated during illumination. In a subsequent verification experiment, nitrification during darkness could be induced in these sediments by purging the headwater with O_2, indicating that the stimulatory effect of illumination on nitrification was indeed caused by benthic micro-algal photosynthetic O_2 production.

However, unlike our understanding of N assimilation, we currently know little about the quantitative importance of benthic micro-algal mediated nitrification and denitrification at the ecosystem level. Until we can develop methods to scale-up these estimates and quantify the role of these processes in the context of total N budgets for systems, we can only speculate.

Applicability to freshwater ecosystems

Traditionally, the role of benthic micro-algae in freshwater ecosystems has been largely ignored. This has primarily been an outcome of the assumption that light penetration to the benthos in these systems was poor and would limit benthic micro-algal distribution and activity. However, in the limited studies that have been conducted, these organisms have proven to be adapted to extremely low light, with the capacity to survive in a light climate of only a few photons (ie. less than 1% of incident irradiance). Preliminary data from freshwater systems indicate significant benthic micro-algal populations, with standing crop estimates ranging from 30 mg m^{-2} to 600 mg m^{-2} for Albert Park Lake, Vic. and Lake Illawarra, NSW, respectively. These data indicate that benthic micro-algal N requirements and the production of O_2 are potentially significant. Thus, in terms of Australian freshwater ecosystems, one of the biggest challenges is to explicitly acknowledge benthic micro-algae in models of N biogeochemical cycling.

Table 1. Modelled estimates of biomass, primary production, turnover and nutrient requirements of benthic micro-algae in Port Phillip Bay over an annual cycle (Light, 1997).

Item	m^{-2}	Bay-wide (1,764 km^2)[a]
Chlorophyll a	27.3 mg	48.7×10^6 g
Carbon[b] (surficial 0–10 mm stratum) (g)	1.4	$2,434.0 \times 10^6$
In situ gross primary production (g C)	67.6	119.3×10^9
Turnover (y^{-1})	49.0	49.0
N requirements[c] (g y^{-1})	11.9	21.0×10^9

[a] Approximately 90% of the total area of Port Phillip Bay (1,950 km^2).
[b] Assuming C : Chl a ratio of 50.
[c] Assuming Redfield Stoichiometry.

Preliminary evidence suggests that the two environment types are operating more or less identically. Thus, what we already know about the role of benthic micro-algae in the biogeochemical cycling of N in the marine environment is directly relevant to freshwater ecosystems.

Knowledge gaps and future research

Irrespective of environment type (freshwater or marine), there exist several key knowledge gaps in our understanding of the role of benthic micro-algae in the biogeochemical cycling of N. We lack detailed information on:

- the interaction between benthic micro-algae and phytoplankton for inorganic N and light;
- the interaction between benthic micro-algae and nitrifying bacteria for NH_4^+;
- the role of benthic micro-algal exudates (cell leakage) in driving microbial processes; and
- the role of increased bio-turbation and bio-irrigation on the cycling of N—such activity may be supported by significant quantities of highly labile carbon introduced to the sediments by benthic micro-algal primary production.

Many of these gaps can be addressed only through a greater integration across areas of algal physiology, microbiology and chemistry.

In terms of further developing our understanding of the role of benthic micro-algae in the cycling of N in freshwater ecosystems, we require information on:

- spatial and temporal dynamics of benthic micro-algal biomass (chlorophyll *a*); and
- rates of photosynthesis and nutrient turnover.

To estimate the quantitative contribution of these processes to the total N budgets of ecosystems (ie. to facilitate gross scaling-up or modelling of integrated estimates) detailed information is required on the functional response of benthic micro-algal photosynthesis, nitrification and denitrification to irradiance.

The factors limiting benthic micro-algal processes may differ somewhat between marine and freshwater environments. While tidal conditions may be a principal factor limiting these photosynthetic processes in marine environments, changes in water level and periods of elevated turbidity may be the most important factors limiting benthic micro-algal activity in freshwater rivers and standing water bodies. Detailed studies of the environmental factors limiting benthic micro-algal photosynthetic processes in Australian freshwater systems are also required.

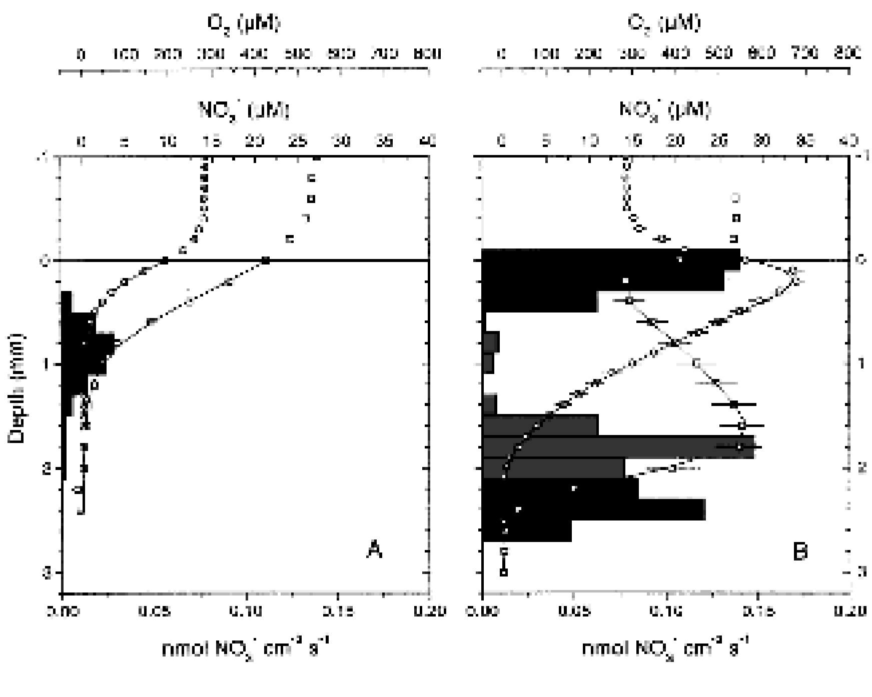

Figure 3. Measured O_2 (circles) and NO_3^- (squares) concentrations, and calculated profiles (lines) for darkened (A) and illuminated (B) sediments colonised by benthic micro-algae. Upper dark bars indicate NO_3^- assimilation, mid light bars indicate nitrification and lower dark bars indicate denitrification. From Lorenzen et al. (1998).

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Macrophytes, nitrogen and N-uptake

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Internal and external processes

Two points need to be emphasised in relation to macrophytes, nitrogen and nitrogen uptake in the context of aquatic ecology. First, the physiology and biochemistry of nitrogen (N) uptake is well-known for terrestrial plants, primarily through research on agricultural species (eg. Marschner, 1986), and has progressed to formulating ecological strategies relevant at the level of habitat and ecosystem. This body of physiological knowledge is a direct introduction to N uptake in freshwater macrophytes. Second, knowledge based on terrestrial plant species is inadequate to understand the role of macrophytes in N cycling in aquatic habitats or ecosystems. Freshwater macrophytes are not a uniform group of plants. Their diverse growth forms (eg. emergent, submerged, floating-leafed, free-floaters) have differing carbon acquisition strategies and different water regime requirements, making it important to specify the type of 'macrophyte' in modelling studies. Like terrestrial plants, freshwater macrophytes modify their immediate environment, and the modifications to the chemical and physical characteristics of their substrate and water column affect N dynamics. These two points relate to 'internal' (ie. within plant)—the main emphasis here—and 'external' (outside plant) processes.

Nitrogen uptake

Most plants take up inorganic forms of N (ammonium, nitrate) by active transport across the cell membrane.[1] Uptake of ammonium is accompanied by simultaneous proton release for charge compensation, and this H^+ excretion lowers rhizosphere pH. Unlike nitrate which can be stored in vacuoles without detrimental effects, both ammonia and ammonium are toxic so must be rapidly converted to amines, amides or amino acids (depending on plant family). These low-molecular-weight organic compounds are the vehicle for transporting N to shoots and leaves via the xylem. In the roots, nitrate must be reduced to ammonia which incurs an energy cost, so it is more efficient for macrophytes to take up ammonium, which is likely to be the dominant form of N in sediments anyway. Assimilation (meaning uptake and conversion) of ammonium in the roots also has a high carbohydrate requirement.

Uptake rates vary between the few macrophyte species that have been studied, even those with similar growth form (Table 1). Whereas it is standard practice to describe N uptake kinetics in terms of a Michaelis–Menten model for algae, this is rare at the whole plant level [2] and the few examples known are for seedlings of well-studied emergent macrophytes such as *Typha* spp. (Dhyr-Jensen and Brix, 1996) and *Phragmites australis* (Romero et al., 1999). Lack of comparative data for freshwater macrophytes means there is little appreciation of their nutrient-ecology, with the exception of well-studied species such as *Phragmites.*

The reducing environment of wetland soils influences various aspects of nutrient uptake, including uptake sites. In emergent macrophytes, nutrient uptake is limited to white roots, ie. those roots with no external lignification and no root plaque deposits, and amongst these roots, it is the laterals that are the most active (Table 1). Submerged macrophytes can take up nutrients from stems and/or leaves as well as roots, and species differ in where

1. A few aquatic plants also use organic nitrogen, but this is unlikely to be the dominant form of uptake. Carnivorous aquatic plants such as bladderwort *Utricularia* spp. capture microfauna; in the tundra, tracer studies have confirmed that some species take up soluble organic nitrogen (Kielland, 1994). Nitrogen-fixing occurs in rhizosphere of several emergent species (eg. Wickstrom and Corkran, 1997).

2. Nitrogen uptake kinetics and macrophyte response (growth) are not as tightly or as immediately coupled as in algae, for three reasons, so need to be modelled accordingly. [1] Uptake sites (usually roots) are separate from growing points (meristems, leaves) and from photosynthetic activity (leaves, stems). Nitrogen must be transported there in a non-toxic form (low molecular weight amines etc.), which is an energy-demanding process. [2] A proportion of carbon fixed is invested in structural and protective compounds, such as xylem, suberin, and to structures for resource acquisition, roots and leaves. [3] Growth can be independent of nitrogen uptake for a short period, when mobilising stored N.

nutrients are sourced, whether water column or substrate (Rattray et al., 1991; Schuette, 1999). The range of responses to nutrient enrichment within three species of submerged macrophytes (Figure 1) emphasises the limitations of using growth form as a robust predictor of plant function, at least in this context. Uptake processes across the cell wall are very well known for non-vascular macrophytes, in particular ecorticate Charophytes because *Chara corallina* has been widely used as a test species in membrane transport research.

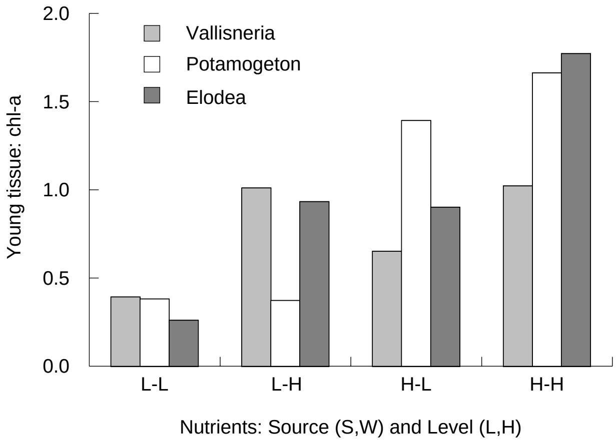

Figure 1. Nutrient source and diversity of submerged macrophyte responses. Growth response of three submerged macrophytes, *Vallisneria americana*, *Potamogeton crispus* and *Elodea canadensis*, to nutrient enrichment of sediment (S) and/or water column (W), using concentration of chlorophyll-a in new tissue. All three respond positively to enrichment of sediment and water (H–H) relative to the un-enriched control (L–L) but differ in the effect of sediment only (H–L) or water column only (L–H). *Vallisneria* responded significantly to water column enrichment, *Potamogeton crispus* to sediment enrichment, and *Elodea canadensis* to sediment and water column enrichment (one-way ANOVA). Drawn from data in Schuette (1999).

Nitrogen uptake is complicated by the highly dynamic physical and chemical characteristics of the soil and water micro-environment around plants. Recent research, mainly on emergent macrophytes, has focused on the plant–environment interactions involving effects of rhizosphere changes in pH, redox potential, and cation exchange and, in particular, the effects of rhizosphere oxygenation. Oxygen leakage from roots (and sometimes from rhizome) results in three distinct micro-environment layers. Closest to the roots is an aerobic zone, where microbial nitrification and organic matter breakdown occurs. Next is the anoxic zone, where the leaked oxygen is depleted but nitrate is still available; if the nitrate is used as an oxidant, gaseous N is released (Brix, 1998) The third layer is the anaerobic zone where organic matter is broken down by fermentation. The width of these zones is variable, being determined by species-specific factors (eg. rhizosphere oxygenation rates) and environmental conditions (ie. factors that drive rhizosphere oxygenation). For one oligotrophic species, *Lobelia dortmanna*, the oxidised zone may be many centimetres thick. Such thicknesses are probably exceptional, and are the result in part of the species having an unusually high root oxygen loss rate, and its highly oligotrophic habitat. A comparative study of eight submerged macrophytes found a 100-fold range in oxygen release rates, with lowest being marine species and highest for species from oligotrophic lakes, and including *L. dortmanna*. The same study found that stream species, which included two known to occur in Australia, *Potamogeton crispus* and *Potamogeton pectinatus*, were intermediate (Sand-Jensen et al., 1982).

In most macrophytes, rhizosphere oxygenation is from leakage as a result of oxygen diffusion but in emergent macrophytes oxygenation rates are higher because of pressurised ventilation or Venturi effects. Internal pressurisation occurs in young green shoots, and is determined by internal–external differences in leaf temperature and humidity. Consequently, flow rates

Table 1. Variations in nutrient uptake within a single growth form. Mean (n=4, with SE in parentheses) rates of N uptake (micromoles H^+ or micromoles N h^{-1} g^{-1} dry wt) for three species of medium-tall emergent macrophytes, in solutions where nitrogen is supplied as either NH^{4+} or NO^{3-}: *Cyperus involucratus*, an introduced species, and *Eleocharis sphacelata* and *Juncus ingens*, both common in riverine wetlands of the southern part of the Murray–Darling Basin.

	Cyperus involucratus		***Eleocharis sphacelata***		***Juncus ingens***	
N as NH^{4+}	H^+	N	H^+	N	H^+	N
All white roots	246 (25)	94 (12)	38 (8)	28 (7)	32 (4)	14 (3)
Laterals only	542 (122)	209 (51)	140 (15)	113 (25)	89 (12)	38 (7)
N as NO_3^-	H^+	N	H^+	N	H^+	N
All white roots	–89 (22)	87 (15)	–25 (8)	10 (3)	–0.8 (4)	6 (2)
Laterals only	–235 (53)	234 (31)	–113 (26)	60 (21)	–8.0 (1)	16 (4)

Taken from Table 3 in Sorrell and Orr (1993).

change diurnally, vary with season and weather, and also in relation to the plant's phenological status. Flow rates down the culm or shoot and rhizosphere oxygenation rates differ widely between species (Table 2). Flow rates are not equivalent to oxygenation rates, and neither is the conversion of pressurisation to flow rates: Brix et al. (1992) have shown that the latter is influenced by a range of species characteristics, such as internal anatomy (lacunae, diaphragm perforations) and mechanical constrictions at the root–shoot junction. Considerable detail is necessary to develop a descriptive mathematical model of within-plant oxygen flow, and to date the most successful model is for *Phragmites australis*. Models of rhizosphere oxygenation would need to add spatially-precise data on root architecture and to quantify root dynamics at a range of temporal scales.

Although the recent literature shows enormous research interest in micro-chemical processes in the rhizosphere of agricultural and wetland plants, most of this (approximately 95%) relates to carbon flux and methane emissions. Very few papers currently consider interactive effects on nutrient (N) uptake and N dynamics, as these topics were a strong research focus a decade ago.

Table 2. Convective flow rates for 14 emergent species. Mean (with SD) convective flow rates as $cm^3 min^{-1} culm^{-1}$ for 14 species, comprising four growth forms. Convective flow rates refer to aerial shoot and are not an approximation for rhizosphere oxygenation rates as they do not account for the resistance at the root–shoot junction.

Species	***Flow rate***
Emergent macrophytes	
Baumea articulata	0.23 (0.06)
Bolboschoenus medianus	<0.01
Cyperus eragrostis	0.02 (0.01)
Cyperus involucratus	0.33 (0.09)
Eleocharis sphacelata	0.85 (0.02)
Schoenoplectus validus	0.29 (0.05)
Typha domingensis	3.41 (0.36)
Typha orientalis	4.44 (0.26)
Phragmites australis	5.20 (0.40)
Juncus ingens	1.17 (0.14)
Heterophyllous macrophyte	
Myriophyllum papillosum	0.04 (0.01)
Surface-leaved macrophyte	
Ludwigia peploides	<0.01
Flood tolerant terrestrials	
Canna sp.	0.06 (0.01)
Arundo donax	<0.01

Taken from Table 2 in Brix et al. (1992).

Macrophytes within the aquatic ecosystem

In an ecosystem context, understanding and quantifying processes involving N and macrophytes must go beyond uptake characteristics, and consider also the 'fate' of N within the plant, as well as the facilitating role of macrophytes (summarised in Table 3). The fate of N refers to how/when/where N is taken up then redistributed within the plant and returned to the environment. This therefore includes the transformation of N from inorganic to organic forms, and its spatial and temporal redistribution through litterfall, underground storage etc. The facilitating role of macrophytes (akin to ecosystem engineers in the sense of Lawton) refers to the environmental changes effected by macrophytes and how these can alter N fluxes. These are outlined in Table 3.

A strategic role

In summary, while macrophytes are not essential to N cycling in the sense that microbes are, they have an important role in providing alternative pathways for N through aquatic ecosystems. Thus, their presence/abundance creates N-cycling diversity and determines N-flux characteristics in a given system. These characteristics could be incorporated in system design and restoration.

Macrophytes and nitrogen: retrospective on Australian research

A historical perspective on freshwater macrophytes and N based on electronic searching with standard databases including StreamLine, but excluding work-in-progress, shows that Australian research is:

Applied rather than strategic

Recent work relating to N uptake by freshwater macrophytes has been strongly driven by resource management issues. Consequently, it is largely descriptive, focused on performance assessment, and addresses whole systems. Exceptions to this are physiological work of Brian Sorrell and Jane Schuette (and possibly some unaccessed university theses).

Limited in scope, sparse through time: not a solid body of knowledge

The few physiological studies of N uptake cover relatively few macrophyte species. No field estimates of N-uptake in Australia were located. There are some estimates for macrophytes in New Zealand: for example, water cress *Nasturtium officinale* is seasonally effective at nitrate removal, reaching a peak N-uptake rate of 1.14 $g m^{-2} d^{-1}$ in early February (Howard-Williams et al., 1982). Interest in eutrophication in the late 1970s–1980s generated single-species studies in laboratory, glasshouse and field of macrophyte responses to N (eg. Cary and Weerts, 1981, 1992; Hocking, 1989). Because these were plant response studies, the variables used (ie. RGR, dry weight, resource allocation patterns etc.) do not cover the 'fate' of N. Nitrogen fate and N use efficiency, using 15N, have been documented only for wetland crop species such as rice, and always expressed relative to 'yield' ie. grain quantity. Only one field study of whole plant annual N budget was located, for *Phragmites australis* (Hocking, 1989). This shows the species to be conservative with respect to N, as 57% of canopy N came from below-ground storage. Effects of eutrophication as N-enrichment on macrophyte communities, on wetland vegetation and the consequences for food webs have received almost no attention. The effect on macrophyte–phytoplankton dynamics is currently being investigated in a large-scale outdoor experiment in northern Victoria.

The role of macrophytes as nutrient (N) pumps has not been quantified in the Australian context, but Australian data for emergent and surface-leaved monocots from three habitats suggest such a 'pump' may be significant, at least in some natural systems. In one year in NSW, *Phragmites australis* took up 67.5 g N m^{-2} y^{-1} from the sediment, and of this dropped 3.8 g N (5.6%) as leaf leachate (ie. soluble N) and 55.5 g N (82%) as organic material (Hocking, 1989). Aquatic stoloniferous grasses such as *Pseudoraphis spinescens*, *Hymenachne acutiglumis*, *Oryza meridionalis* may be contributing as much as 183.6, 202.1 and 33.0 kg N to each hectare of floodplain surface annually (Finlayson, 1991). In the littoral zone of an estuary in Western Australia, *Juncus kraussii* is assumed to be pumping 5.2 g N m^{-2} y^{-1} (Congdon and McComb, 1980). In contrast, litterfall has been relatively well-studied, notably for riparian and coastal trees. Characteristics such as quantity, timing, variability and forms have been estimated for a range of habitats (upland streams, terminal wetlands, coastal wetlands, tropical floodplains) and for a range of species (*Casuarina glauca*, *Melaleuca* spp., *Eucalyptus camaldulensis*).

Macrophytes and nitrogen: outside Australia

Four research themes dominate international research on N uptake and macrophytes: (1) understanding N use patterns at species, community and ecosystem level; (2) dieback of *Phragmites australis*; (3) effects and consequences of N enrichment; and (4) macrophytes as indicators (phytometers, and N:P ratios). This paper is limited to (2), which is a specific subset of (3), and (4).

Table 3. Macrophytes and nitrogen fluxes

	Internal–external	***'Facilitates'***
Nitrogen transformations	UPTAKE & INCORPORATION: inorganic to organic. Also N-FIXATION: RARELY: Organic forms taken up	MACROPHYTES AS SUBSTRATE for epiphytes, bio-films etc: This can lead to localised N-fixation on plant parts in water column. OXYGENATION OF RHIZOSPHERE
Spatial re-distributions	NITROGEN (NUTRIENT) PUMP: from sediment to plant canopy / to water column or sediment surface, by uptake, leaching, litterfall. If litterfall, then mobility is increased, spatial re-distribution more important though transport, foodweb uptake, and likelihood of export increases.	SPATIAL & TEMPORAL ARE LINKED, mainly through system hydrology (residence times, water regime, events) MACROPHYTE BEDS AS HABITAT, NURSERY, REFUGE: accumulation of organic N until flushed out MACROPHYTE BEDS AS ACCUMULATION POINTS: are low-flow patch in lotic system; accumulation point for litter, both autochthonous and allochthonous until flushed out.
Temporal re-adjustments	UPTAKE THEN EITHER STORAGE OR LITTERFALL: in perennials, rates are temporally offset –spring v summer–autumn WHOLE PLANT: mean residence time for N shows species differences are greater than resource differences, eg. *Carex* RARELY: bypassing the mineralisation step in Arctic tundra is an acceleration 'short circuit'	

Phragmites dieback in Europe

Two international research programs involving nine member countries, EUREED in 1993–94 and EUREED II in 1996–99, have been funded by the Environment and Climate program of the European Commission. The management issue—dieback of *Phragmites australis* — has driven a huge research program involving physiology of plant nutrient requirements and carbohydrate utilisation, ecotypic and morphologic diversity, development and anatomy, modelling, and plant–environment relations. The results are proving challenging, with a strong emphasis on N. For example, ecologically significant ecotypes—known as 'assimilation' and 'translocation' types—with differing growth and nutrient cycling have been identified, and are. The former are adapted to high nutrient sites. Predicting the effects of eutrophication may thus depend on understanding not just species responses but also ecotype characteristics. Another example is that dieback sites are characterised by lower decomposition rates and hence accumulate plant litter. The resulting concentrations of certain 'phytotoxins' (organic acids) adversely affect plant growth because they cause distorted growth at critical developmental stages in underground parts. As a result, there is a strong management recommendation that reed-beds should have a lowered water level once per season to allow oxidation of phytotoxins and encourage aerobic decomposition. which encapsulates the notion that dieback is an interactive result of eutrophication and water management. Such a recommendation is very relevant to Australia where modifications to water regime are widespread.

Phytometers, N:P ratios

N:P ratios in canopy tissue of emergent macrophyte tissues are being strongly advocated and used overseas (eg. in the Everglades) as a 'new' 'tool' to detect and diagnose nutrient (ie. N, or P, or N and P) limitation for the plants (Koerselman and Meuleman, 1996). What is relatively 'new' in this particular application of N:P ratios is their relatively strong empirical base (40 field experiments) combined with the inverted approach ie. assessment rather than prediction. Such an approach could have potential as a rapid survey or site-selection technique. However, there are certain limitations (Roberts, 1999). For example, only one growth form (emergent macrophytes) gives reliable and consistent results. The use of tissue N:P from other growth forms, especially submerged macrophytes (Figure 1) does not give consistent answers between species. Also, the information base is quite specific: emergent macrophytes indicate sediment conditions for emergent macrophytes. Using two sets of N:P data from Australian studies (Hocking, 1989; Congdon and McComb, 1980) and following Koerselman and Meuleman (1996), shows that growing conditions beside an irrigation drain near Griffith (Figure 2) were N-limiting for *Phragmites australis*; in contrast, the littoral zone of Blackwood estuary was P-limiting for *Juncus kraussii* (not shown). Although only two points, both are contrary to commonly-held generalities, and so contribute to the increasing body of evidence that paradigms re nutrient limitation (N or P) with respect to habitats and ecosystems need to be re-evaluated.

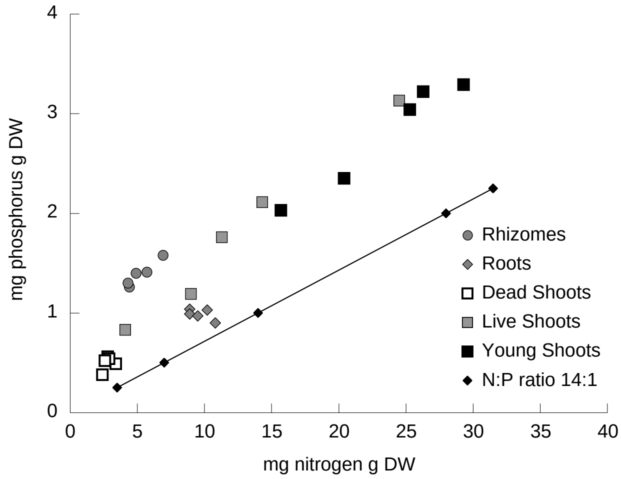

Figure 2. Tissue N:P diagnosis of growing condition. Growing conditions defined as N-limiting for a slightly eutrophic, highly modified creek in New South Wales, based on tissues of *Phragmites australis* collected at various times through the year, and showing consistency of N:P ratio for a range of live and dead tissues. Trend line is for mass N:P = 14 (following Koerselman and Meuleman 1996).

Future directions

Disturbed and modified habitats and ecosystems

At least in eastern Australia, it is clear that 200 years of European settlement of the continent have changed the abundance, species composition and regeneration potential of plant communities in aquatic systems, principally through introduced species and water management practices. Nonetheless, cattle pugging, carp bioturbation of sediments, loss of macrophyte communities (for whatever reason) and changed vegetation structure have not been much considered in relation to N fluxes. Their combined effect is likely to a simplification in the number of N pathways and forms of N; and the consequences are probably a more rapid flux of available N.

Emergent properties

Australia has a small base in freshwater macrophyte ecology and physiology, so does not have much capacity to build a suite of species-specific studies and lay a solid if conventional knowledge base. The alternative approach, and one suited to large-scale resource issues, is to focus on the habitat or ecosystem level. Building on and testing the synthetic conceptual ideas currently being formulated mainly in the northern hemisphere and mainly in relation to terrestrial vascular plants, is a real option. The emergent properties of plant communities (eg. describing dynamics of plant communities in reductionist terms of broad-based resource acquisition strategies) could be used in a strategic sense to predict likely outcomes of resource shifts, such as eutrophication or N-enrichment.

Field assessment of nitrogen limitation/ enrichment

The phytometer approach of Koerselman and Meuleman (1996) is a tool that could be readily used to make broad-scale first pass assessment of habitats, ecosystems and situations where N is or is not limiting, and so identify where N-sensitive water management practices would need to be implemented.

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Nitrogen and cyanobacteria in Australian lowland rivers — unanswered questions

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Introduction

Historically, phosphorus (P) has been viewed as the element that limits production in freshwater systems, but some critical reviews of historical data have suggested a more influential role for nitrogen (N). For example, Smith (1982) concluded that the availability of total N influenced the concentration of chlorophyll, even in lakes where P alone appeared to be limiting. Additionally, Elser et al. (1990) in a review of North American lakes found that the frequency of N-limitation was equivalent to that of P, although some of these observations may reflect the techniques used to determine limitation.

Phosphorus should be the element limiting phytoplankton yield in freshwater systems. Low inorganic N concentrations should still allow the growth of cyanobacteria which can fix atmospheric N and thereby utilise P until it eventually becomes limiting. However, cyanobacteria can dominate only under particular physical conditions, generally low flow and thermal stratification. If physical conditions do not favour N-fixers, N may limit overall phytoplankton growth and yield in mixed systems.

The phytoplankton community can be divided into two categories: a larger category of which the members are entirely dependent upon dissolved sources of N; and a much smaller sub-group of cyanobacteria, which can electively fix atmospheric N when dissolved sources are diminished. Evidence has begun to emerge that the form of inorganic N may also play an important role in species selection of non-N_2-fixers. In general NH_4^+ is thought to be utilised readily by both cyanobacteria and micro-algae, while NO_3 supports eukaryotic micro-algae (Blomqvist et al., 1994).

The various components of the N cycle are well documented, but the relative contributions of these components in the dynamics of phytoplankton in Australian rivers are largely unknown. There is growing evidence that N may be limiting in Australian systems, and rapid techniques are becoming available to accurately identify potential nutrient limitation (eg. Wood and Oliver, 1995). As the tools become available, the right questions to tackle become paramount. This discussion will focus on questions regarding the availability and use of N, the relative importance of differences in N-acquisition by cyanobacteria. We will draw on our observations of phytoplankton populations in the lower River Murray, as a case to highlight some of the issues that may be important in understanding nutrient cycling and algal ecology in such systems.

Does nitrogen availability determine which cyanobacteria dominate in Australian lowland rivers?

Baker et al. (1993) conducted a survey of cyanobacterial distribution and abundance within the Murray–Darling Basin. Of the 630 water or scum samples analysed, 72.4% were dominated by *Anabaena* spp., whereas *Microcystis* spp. were dominant or co-dominant in 18.2%. In reservoir samples, *Microcystis* spp. were dominant or co-dominant in 52%, while *Anabaena* achieved dominance in 96% of reservoir samples. In samples collected from rivers, 88% of samples had *Anabaena* spp. as a dominant taxa, while *Microcystis* spp. were dominant in only 17%.

The prominent and immediately obvious difference between *Anabaena* and *Microcystis* is that *Anabaena* is able to fix N_2-nitrogen. Thus, these observation would suggest that N fixation has a significant role in N acquisition by riverine cyanobacteria, and therefore in the N cycle in Australian rivers, particularly during summer and early autumn. Acquisition of the different forms of N follows a well defined order; ammonium is utilised before nitrate and supply of both must be limiting before N_2 is fixed, as N fixation is an energetically expensive process. Chemical analyses of N forms in water may therefore provide a pointer as to the potential need for N_2-fixation by cyanobacteria. Although N-fixation appears to be important, there has been no direct measurements of N_2-fixation by cyanobacteria in Australian rivers. However, observations of heterocyst occurrence in a variety of riverine *Anabaena* spp. support the suggestion that N_2 is being fixed when nitrate and ammonium concentrations are low.

Sherman et al. (1998) developed an argument for evidence of N_2-fixation in the Murrumbidgee River. They observed that during a low-flow period, *Anabaena* grew rapidly, total P declined as particulate material settled, but the total N concentration tended to increase. It was suggested that this increase in total N was the result of N fixation by *Anabaena* at a rate of 0.37 pg N cell^{-1} day^{-1} (Sherman et al., 1998). Estimation of the rate of N fixation assumes that 100% of the total N increase was from N fixation and there was no flux of N from other sources or redistribution of phytoplankton. Assumptions such as this cannot be demonstrated without direct measurements of N sources and sinks in Australian rivers, which at present are inadequately addressed.

Observations from the lower River Murray

Baker et al. (2000) tracked time-aligned parcels of water in a reach of the lower River Murray and calculated growth of the dominant species. Mean growth rates of *Anabaena circinalis* and *A. flos-aquae* were 0.176 and 0.132 day^{-1}, respectively. However, maximum cell densities were, respectively, 2670 and 4560 cells mL^{-1}, which suggests that nutrients or grazing were limiting phytoplankton yield. It is possible that N_2-fixation was limited by light under mixed conditions but increased with increasing light exposure as buoyant cyanobacteria floated towards the surface during calm periods (Stal-Lucas and Walsby, 1998).

During the summer of 1995–1996 nutrient growth bioassays and FDA-conversion bioassays revealed N limitation on several occasions in the lower River Murray and the N present was essentially unavailable for growth. In contrast, P limitation was detected on only one occasion and between 8 and 70% of the total P was bioavailable.

We suggest that although P may ultimately limit total phytoplankton biomass, low N concentrations in the River Murray favour heterocystic N-fixing species such as *Anabaena circinalis* and *Anabaena flos-aquae* while limiting the growth capacity of non-N fixing species such as *Microcystis aeruginosa*. Physical conditions in the lower River Murray during summer are similar to those that favour growth of *Microcystis* (Ganf, 1974), but populations of *Microcystis* did not become established during the study period. The particular combination of physical and chemical conditions presumably favoured the growth of *Anabaena* in preference to non-N fixing cyanobacteria, albeit at sub-optimal conditions.

During the study period, most of the water in the lower River Murray was sourced from the upper Murray and its tributaries, which historically have lower nutrient loads than the other major tributary, the Darling River. In the summer of 1996–97, a higher contribution of Darling River water resulted in elevated levels of both N and P in the lower River Murray and consequently the non-N fixing cyanobacterium *Planktothrix perornata* was found in relatively high abundance (Baker, 1999).

A conceptual model, based on the findings of this study and also on the study by Bormans et al. (1997), has been developed to summarise the physical and chemical factors governing the abundance of cyanobacteria in the lower River Murray (Figure 1). We rank flow as the primary factor affecting the development of cyanobacterial populations. High flow (>10,000 ML d^{-1}) results in high turbulence and species such as the diatom *Aulacoseira granulata* are favoured. When flow is moderate (ca. 10,000 ML d^{-1}), diurnal stratification occurs if wind strength is low (<1.2 m s^{-1}). During periods of low flow, equivalent to summer entitlement flows (4,000 ML d^{-1}), turbulence is sufficiently low to allow some degree of thermal stratification, provided that wind strength is low to moderate (<3 m s^{-1}). Persistent stratification may result when wind speed is less than 1.2 m s–^{1} (and flow is low), while diurnal stratification is more likely at wind speeds between 1.2–3 m s^{-1}. Irrespective of flow, high wind speed (>3 m s^{-1}) will disrupt thermal stratification and result in a mixed water column.

In the model, the source of water is the other environmental factor affecting algal dynamics. If water is sourced from the Darling, or if over-bank flooding has occurred during the high spring flows originating from the upper River Murray, P concentrations may increase. When P concentration is high, N availability will then determine which species composition occurs. High soluble inorganic N availability favours non N_2-fixing cyanobacterial genera such as *Microcystis* and *Planktothrix* and other phytoplankton. However, if N availability is low, N fixing genera, such as *Anabaena*, *Aphanizomenon*, *Anabaenopsis* and *Cylindrospermopsis* obtain a comparative advantage. If river flow originates from the upper River Murray and flow remains within the main channel, available P will be low and consequently phytoplankton abundance will remain low.

Harris et al. (1996) extrapolated their denitrification measurements to estimates of bay-wide denitrification rates in Port Phillip Bay. The N budget of the whole bay indicates efficient removal of N from the waters by phytoplankton, and the subsequent elimination of N by bacterial denitrification is a mechanism by which the bay is prevented from becoming eutrophic. It is not known how universal this process is in Australian freshwater

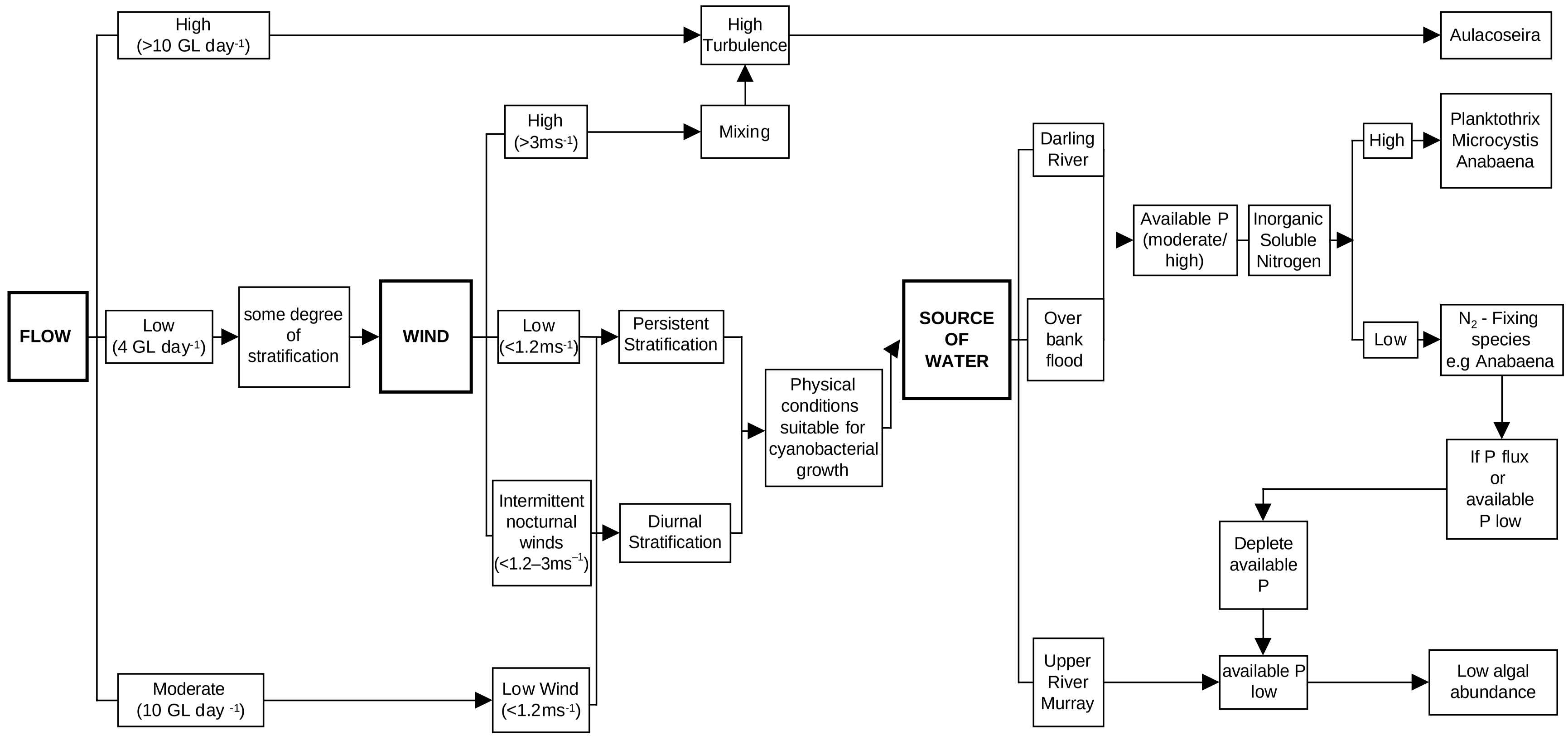

Figure 1. Summary of the physical and chemical factors governing the abundance of cyanobacteria in the lower River Murray

systems, or the relative importance of benthic algae in facilitating N removal. The evidence suggests that during some years the lower Murray may act in this manner but recent work on a shallow urban river (the Torrens Lake, South Australia: G. Ganf, J. Brookes, L. Linden, C. Hodgson, and M. Burch, unpublished data) suggests that sudden discharge of nutrient-rich water, from either external or internal sources, into an ideal physical habitat may promote the rapid formation of algal blooms.

How important is pulsed nutrient supply to phytoplankton ecology and population growth in low-nutrient systems?

Harris (1994) states that "... in Australia, phytoplankton dynamics are dominated by irregular and infrequent extreme events". Nutrient input can be associated with rain events or sediment flux which tend to be irregular, or with point-source effluent inputs, which may be more regular. The impact and importance of pulsed nutrient supply may not be apparent in rivers because populations are carried downstream. In the lower River Murray in South Australia, most (95%) of the water originates from the eastern states and the river is highly regulated. However, discrete populations of *Anabaena* spp. have been observed migrating downstream and the events which either triggered or accelerated the population growth are unknown. An example of the impact of 'episodic events' on phytoplankton growth, which may be more readily observed in smaller systems where relatively small events have noticeable impacts, occurs in an unpublished study of G. Ganf, J. Brookes, L. Linden, C. Hodgson, and M. Burch. This study showed that pulsed nutrient supply, caused by both sediment release and a rainfall event, enabled nutrient uptake which sustained a *Microcystis aeruginosa* bloom, even when ambient nutrient concentrations declined below detectable levels.

What is the role of intracellular nutrient storage in cyanobacterial population growth?

Nutrient status of phytoplankton in a water-body is determined not only by the ambient concentrations of the various nutrients but also by cellular uptake rates and storage capacity. Cyanobacteria are able to store P as polyphosphate and N as either phycocyanin or cyanophycin. However, growth rates and yield attainable using internal cellular reserves vary considerably. Laboratory grown, nutrient-replete cultures transferred into P-free media can display positive growth for several weeks. In contrast, nutrient-replete cultures transferred into N-free media maintain growth for much shorter periods (days). The vastly different phytoplankton yields obtainable from intracellular stores of either N or P must be considered when attempting to interpret results from growth bioassays.

Different storage capacities of N and P by phytoplankton have significant implications for the influence of ambient supply rates of N and P on growth. If P supply is irregular, it is unlikely to affect algal growth to the same extent as an irregular N supply. Cyanobacteria which are able to fix N_2 have an advantage in a riverine environment with either low or irregular N supply, but as the results from the lower Murray would indicate, this does not necessarily result in the development of large populations. One explanation for relatively low population yields could be that the range of riverine *Anabaena* cannot capture sufficient energy in turbid environments to support N_2-fixation.

If the N requirements of cyanobacterial cells are not met, cellular functions such as gas vesicle production and photosynthetic capacity decline further, decreasing the ability to respond to stratification events and maximise light capture. This raises several questions:

Is N_2-fixation by *Anabaena* limited by light availability in turbid environments except during periods of persistent stratification?
Is sufficient N stored to enable growth when N-fixation is low or is this process also limited by carbon availability?
What is the critical light dose required to fix sufficient N to satisfy all cellular requirements and how does this differ from the critical light dose required when inorganic N is abundant?
If inorganic N is abundant can *Anabaena* tolerate more frequent or deeper mixing?

These questions indicate that there is a range of interdependent rate-limiting processes which will determine the population yield of N fixing cyanobacteria in a dynamic riverine environment.

Do zooplankton have a role in phytoplankton dynamics in rivers?

There may be relationships between zooplankton, phytoplankton and N, in addition to preferential grazing and simple recycling of nutrients, which require further investigations. MacKay and Elser (1998) tested the hypothesis that differential recycling of N and P by *Daphnia* affects the physiological status of cyanobacteria. *Daphnia* have high P requirements (low body N:P ratio) and tend to sequester more P than N. Consequently, in an experimental trial they found that when *Daphnia* was present in lake water, NH_4 concentrations increased relative to P and there was a considerable reduction in N_2-fixation. Thus, by differentially recycling N relative to P, *Daphnia* may reduce the advantage that N-fixing cyanobacteria have over other phytoplankton. Similar processes may be operating to influence nutrient dynamics in lowland rivers contributing to low cyanobacterial abundance, but the dearth of studies into phytoplankton–zooplankton interactions does not allow us to assess their relative importance.

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