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A Nutrient Dynamics Model for Australian Waterways:

Land use, catchment biogeochemistry and water quality in Australian rivers, lakes and estuaries

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Glossary

algal blooms	a sudden proliferation of microscopic algae in water bodies, stimulated by the input of nutrients such as phosphates.
allochthonous	Organic material that is developed or derived outside a particular waterbody.
anoxic	oxygen deficient.
aquatic ecosystem	all living and non-living elements, and the relationship between them, of a water-based environment.
benthos	plants and animals living on the stream bottom.
biodiversity	the variety of life forms, the different plants, animals and microorganisms, the genes they contain and the ecosystems they form.
biofilm	layer of materials created by microorganisms on an underwater surface
biogeochemical	the movement of chemical elements between organisms and non-living compartments of atmosphere, aquatic systems and soils.
catchment	the area of land drained by a river and its tributaries.
cyanobacterial blooms	blue-green algal blooms.
dryland salinity	salinity caused when the replacement of native vegetation with crops and pastures that have shallower roots and different water use requirements, leads to more water flowing into groundwater system and the increased mobilisation of salt. This saline water rises to near the ground surface in low-lying areas or at the break of slope, and/or flows underground directly into streams.
ecosystem	communities of organisms and their physical environment interacting as a unit.
embayment	bay or formation resembling a bay.
estuary	area of an inlet or river mouth that is influenced by the tides and also by fresh water from the land; area where fresh and salt waters mix.
eutrophication	process by which waters become enriched with nutrients, primarily nitrogen and phosphorus, which stimulate the growth of aquatic flora and/or fauna.
exceedences	those times a measurement of a component goes beyond a specified limit.
flow regime	pattern of water flow in a river or stream. In undeveloped rivers and streams flow regimes are related to climatic conditions. In regulated rivers (i.e. dammed rivers), flow regimes are often altered from natural patterns.
ground water	water that occurs beneath the ground held in or moving through saturated layers of soil, sediment or rock.
hydrologic	relating to the distribution and movement of water.

hypolimnion	the region of a waterbody that extends from below the thermocline to the bottom of the lake; it is thus removed from much of the surface influence.
impoundment	reservoir or dam
indicators	any physical, chemical or biological characteristic used as a measure of environmental, social or economic conditions.
iron complex	iron bound with other molecules.
Kjeldahl	a method for the quantitative estimation of nitrogen in organic compounds.
landscape	an area of land and its physical features. A term used to describe an area that has common features.
macrophytes	aquatic plants such as reeds and bull-rushes.
microhpytobenthos	microscopic plants living on the stream bottom.
microorganism	any organism of microscopic size.
oxic	sufficient oxygen
peatland	wetland ecosystem in which organic matter is produced faster than it is decomposed, resulting in the accumulation of partially decomposed vegetative material called peat.
pedology	the study of soil.
pelagic	ecological zone that includes the entire water column.
phytoplankton	small (often microscopic) aquatic plants suspended in water.
ponding	accumulation of a small body of water.
recharge	the portion of rainfall or river flow that percolates down through the soil and rock formations to reach the groundwater.
riparian vegetation	plant communities on the fringes and adjacent to water bodies.
runoff	portion of rainfall not immediately absorbed into the soil and which becomes surface flow.
salinity	the concentration of sodium chloride or dissolved salts in water, usually expressed in electrical conductivity (EC) units or milligrams of total dissolved solids per litre (mg/L TDS).
sodic soils	soils with a high proportion of sodium relative to calcium, potassium and magnesium in the composition of the exchangeable cations on the clay fraction.
stoichiometry	proportions in which elements are combined in compounds.
suspended solid	any solid substance present in water in an undissolved state, usually contributing directly to turbidity.
sustainable	an activity able to be carried out without damaging the long-term health and integrity of natural systems.
turbidity	a measure of the extent to which the passage of light through water is reduced by suspended matter.
wetlands	land areas along fresh and saltwater courses that are flooded all or part of the time, leading to the development of a

characteristic suite of plant and animal communities and determining the type and productivity of soils.

Executive Summary

Many natural habitats of Australia have been fragmented through land clearing. Rivers have been extensively dammed and their flows controlled. Much surface water is extracted for irrigation and urban supplies. This paper analyses the effects of this resource use by explicitly linking water quality data from State archives with land use. The analysis uses catchment biogeochemistry to illustrate the impact of land use on the movement of major ions and nutrients from the landscape and finds important relationships between land use, habitat fragmentation and water quality. These insights will influence how the Australian landscape is managed and restored.

Land clearing leads to far reaching cumulative, though non-linear deleterious changes to soil properties, vegetation and surface and ground water quality and quantity. At around 50% clearance, there is a sharp increase in export of salinity, suspended solids and nutrients to the waterways and groundwater (although not suspended solids for groundwater) with a corresponding decline in water quality. Stream power is related to slope and rainfall intensity so that once slopes are cleared the surface run off has sufficient power to begin to cut down into the soil and subsoil.

The increased problems stem from increased surface runoff and seepage to groundwater due to the reduced vegetation less effectively impeding water flow or retaining nutrients and particulates. It appears that deleterious changes will occur regardless of how sensitively the land is cleared, eg if care is taken to minimise erosion while clearing, changes will still occur, though perhaps less severe for suspended solids. Changes such as increased salinity can occur quite quickly, eg a few years to a decade after clearing. This has clear implications for the current high rate of clearing in parts of Australia.

This steep increase in runoff and export of nutrients, salinity and suspended solids after 50% clearance has considerable implications for Nation Action Plan for Salinity and Water Quality / Natural Heritage Trust (NAP/NHT2). The main implication is that meaningful NAP/NHT2 targets to improve water quality and landscape function should ideally aim to correct hydrological imbalances, likely to involve the equivalent water use of around 50% tree or possibly other deep rooted vegetation cover. Otherwise NAP/NHT2 targets, unless modest or interim, are unlikely to be met. Because of possible local effects, eg soils, topography and type and distribution of vegetation cover, it may be possible in some areas to get improvements to catchment exports and water quality at a somewhat lower percentage of

deep rooted vegetation cover. The most appropriate targets could be determined by data and research on the best plant species (eg high water use) and their placement in the catchment, biodiversity goals and farming and grazing systems.

Compared with many other countries, Australia has low export of nutrients from catchments. This is due to the low rainfall, low relief, low fertiliser usage, low nutrient status of our soils, low population and lack of atmospheric deposition of nutrients (such deposition is a problem in Northern Hemisphere countries).

Aquatic ecosystems exist in two states, either clear and macrophyte dominated or turbid and plankton dominated. The switch between the two states is often abrupt and the ecosystem response to perturbation is highly non-linear and complex. The characteristic response shows strong hysteresis, which is when the ecosystem state shifts from one state to the other (eg clear to turbid) and is highly resistant to switching back. A waterway in a well vegetated catchment with clear water and dominated by macrophytes becomes replaced by turbid, more saline water that is algal dominated after clearing. Much of inland Australia corresponds with this situation. Ecosystems can show “critical loads” or “points of no return” which are of great concern for managers.

It is still possible to save many estuaries and coastal lagoons. Many estuaries are seasonally nitrogen limited and increased inputs of nitrogen from fertilisers, urban runoff and clearing, could impair estuarine water quality and cause seagrass loss through phytoplankton and epiphytic growth on the seagrass (seagrass is important for fish breeding). As long as abundant seagrasses are present, Australian estuaries have good water quality and nitrate is usually almost unmeasurable. Like impoundments, N:P ratios in surface waters are very low. In some cases, estuaries may also become phosphorus limited. The Port Phillip Bay study by CSIRO used the concept of interactions of the main biological groups to explain the behaviour of the bay and formulate recommendations for management.

Many rivers are past the point of no return unless very large amelioration is undertaken. Once the waterways become saturated with respect to incoming salts, nutrients and suspended solids, problems, such as a decline in in-stream biota become apparent. Such problems can be partly mitigated by measures to reduce erosion and prevent rise in groundwater levels.

Water quality in rivers is a function of land use and catchment geology as well as in-stream interactions, including position in the overall landscape pattern of regulated reaches, reservoirs and wetlands. Land use change in Australia has tended to increase flow regulation and the number of impoundments and weir pools of various kinds. Australia is losing wetlands rapidly because of flow regulation and drainage, which is a further problem for waterways and biodiversity.

Water quality reflects land use in other ways, eg sodicity and acidity of soils. Most Australian soils are poorly buffered and tend to be made acidic by the clearing of the land and extensive use of legumes such as sub clover, which generate nitrate in the soil profile, and certain fertilisers such as ammonium sulphate. Calcium leaching is associated with acid deposition and acidity alters the chemistry of both ground waters and surface waters. The acid sulphate soils of many Australian coastal areas are a special case and when disturbed can generate serious acid and heavy metal pollution of soils and waterways, with resultant loss of aquatic species including fish and infrastructure damage.

Salinity is a good indicator of perturbed major ion chemistry and, because the movement of ground water through the soil profile is a good integrator of the effects of land clearance and agricultural development. Ground water influences on water quality were clearly higher in cleared catchments.

Water salinity is not, however, a good predictor of other biologically relevant indicators of water quality (eg N and P). It is necessary to understand the forms, fluxes and transformations of N and P in catchments if we are to formulate a more complete theory of catchment biogeochemistry and its application to management questions. Dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) are better nutrient indicators than total nitrogen (TN) and total phosphorus (TP) and the ratio of DIN to DIP is a good predictor of algal blooms. They are constituents of TN and TP respectively and easier to measure than TN and TP. This does not preclude also measuring TN and TP.

The combination of flow regulation, impoundment of rivers and removal of wetlands has had a major effect on the ecology of Australian rivers. Clearance and land use change, increased erosion and increased sodicity, have flipped many Australian rivers from clear and macrophyte dominated, to turbid and plankton dominated. These effects are probably no longer reversible without massive, and unrealistic, landscape rehabilitation. While the rivers have been largely lost, most Australian estuaries are not yet past the “critical load” point.

We should, therefore, take a landscape approach to understanding and managing water quality from hill-slope to estuary. Removal of more than 50% of the native plant cover results in increases in both the horizontal and vertical flows, so that runoff increases after rain and ground water becomes a more important influence on stream chemistry during low flow periods. Across wide areas of this continent stream salinity is a good integrator of the effects of landscape change in the catchment.

It is not just dryland salinity that results from land clearing. Changing land use over quite short time scales alters many aspects of water chemistry. Agricultural practices lead to soil acidity and sodicity, both of which are visible in the stream chemistry. To restore water quality and river ecology it will clearly be necessary to restore the land and its ecological function.

Introduction

For many years the true value of Australian water quality data has been underestimated. While most of it has been used in the context of compliance with ANZECC water quality criteria, other interpretations are rare. Indeed, proverbial tales of the variability of the data and of samples "left on a truck out the back of Burke for days" have seen many of the data dismissed as meaningless and left unanalysed. Furthermore, sampling effort has been wound back in many States because mere monitoring without analysis or apparent meaning is not popular in an atmosphere of outcome budgeting and of financial strictures.

This paper is an effort to provide context and meaning for these important data in the hope that they will shed light on some critical aspects of land use and sustainability on this continent. Further it is hoped that this report will stimulate others to analyse the data and to collect more in the future. If we have some idea of the proper questions to ask of these data, then meaning will be found and effort can be better targeted and even increased.

These data should also to be seen in the light of the considerable effort that has been put into such programs as the monitoring of river health using data on the presence and absence of particular groups of macro-invertebrates (Marchant et al. 1999). This type of analysis, which began with RIVPACS in the United Kingdom (Wright 1995) and was developed into the AUSIVAS program (Smith et al. 1999, Turak et al. 1999), now has about 6000 sampling sites around Australia and has revealed much about river health (see the special issue of Freshwater Biology 41(2) 1999). In the RIVPACS methodology it is possible to identify river reaches that have been impacted by anthropogenic or other change, but the data provide neither much of a guide as to what precisely the impact was, nor a guide for improved management (but see Faith and Norris (1989) for an analysis of this kind).

What I seek here is analysis of the water quality data (most of it contained in State monitoring reports), which can explicitly be used to link land use to water quality. To this end the analysis takes the form of an exploration of catchment biogeochemistry, in the form of assessments of the impact of land use on the movement of major ions and nutrients from the landscape, through rivers, streams and impoundments to estuaries. I will argue below that such an analysis is not so complicated as it may seem – the physiology of the catchment, impoundment or estuary being merely the sum of the physiologies of the component species. To explain the approach, and to provide some necessary background, it is necessary to outline some basic ecological theory.

As part of these analyses I have tried to assess what measures of water quality might make good indicators; ie what measures of water quality provide robust indications of functional links and guides to management action.

Some background ecological theory

What we have done in Australia is one of the world's largest habitat and landscape fragmentation experiments. Since the arrival of the first white settlers we have systematically cleared large areas of the continent and replaced the native bush with western agricultural crops and farming practices. We have fragmented the natural habitats of Australia, destroying biodiversity and changing ecosystem function in the process. We shall need to examine the relationships between habitat fragmentation, biodiversity and ecosystem function if we are to explain the impacts of these practices on our rivers and surface waters.

To water our crops we have extensively dammed the rivers and controlled their flows. Much surface water is extracted for irrigation and urban supplies. Because Australia has one of the world's most variable rainfall and river flow patterns, certainty of supply must be guaranteed by the construction of huge impoundments. The ponding of water in the landscape and the regulation of river flows have provided certainty of supply but has drastically changed the ecology of our major rivers (Puckridge et al. 1998).

Land clearance and river regulation have changed the ecology of Australia considerably in the last two hundred years. We shall have to consult both the Australian and the international literature if we are to provide a conceptual framework that will lead us to an interpretation of the impact of land use on the water quality data from our rivers.

Harris (1994, 1996) discussed the role of nutrients in stimulating algal blooms, the use of mass balance models and the biogeochemistry of nitrogen (N) and phosphorus (P) in Australian catchments. In particular, Harris (1996) criticised the use of total N (TN) and total P (TP) and their ratios as management tools. It is necessary to understand the forms, fluxes and transformations of N and P in catchments if we are to formulate a more complete theory of catchment biogeochemistry and its application to management questions.

Over the last thirty years I have written a series of papers that have attempted to understand the workings of ecosystems from a mechanistic perspective (see Harris 1997, 1998, 1999a,b, 2000, and references therein). Ecosystem function is seen as being controlled by the sum of the species properties and interactions (a “bottom up” approach), rather than as a product of some “goal function” of the system as a whole (Jorgensen 1999). This is important as it allows an explanation of many ecosystem properties and observed phenomena. Indeed, if we look upon a series of catchments which have been partly or completely cleared as a series of experiments on the effects of land clearance on water quality, then provided we have some understanding of the physiology of the dominant terrestrial and aquatic species, some measurements of water quality, hydrology and some estimates of land, use we can make much progress in analysing the outcomes.

The mechanistic approach also allows us to analyse the effects of habitat fragmentation and the consequent reductions in biodiversity on landscape and catchment physiology. We begin by assuming, for the sake of argument, that before the coming of western people to Australia, a long term equilibrium had evolved between the climate, the geomorphology, the water balance, the nutrient cycling and the natural ecosystems of Australia (see eg Specht and Specht (1999) and the modelling study of Schimel et al. 1997). This would have been a situation similar to that proposed by Eagleson (see discussion and references in Hatton et al. 1997) wherein by a long-term series of invasions, interactions and evolution, resource use was balanced and optimised. Loreau (1998a, b) explained the underlying processes through modelling ecological successions and showed that interactions between and within functional groups of organisms (eg trees, shrubs, herbs etc.) would have produced something close to a long term optimal water and nutrient use efficiency. As I have argued however (Harris 1999b), climate variability would have ensured that the result obtained was never totally optimal because of the difficulties of tracking ever-changing resource availability.

Fragmentation of the original landscape caused loss of biodiversity and function. It is clear from recent ecological experiments and observations (Chapin et al. 1998, Tilman 2000) that there are some not so complex interactions between biodiversity and ecosystem function. Increased biodiversity increases the ecological functionality, increases productivity and reduces leakage of water and nutrients (see Hector et al. 1999, McGrady-Steed and Morin 2000, Symstad et al. 1998, Tilman 1999, Tilman et al. 1997, Yachi and Loreau 1999). Tilman (2000) likens the situation to that of “snow balls on a barn door”. Each species has somewhat different functional attributes so that as biodiversity is increased (and the number of snowball splatters on the door increases) greater and greater coverage and increased resource use efficiency is achieved.

The observed increases in productivity and water and nutrient use efficiency as biodiversity is increased (Specht and Specht 1999) suggest that there is functional diversity and complementarity between the species. Functional aspects of the ecosystem would not improve with increased biodiversity unless there was an additive effect on function as well as species number (Chapin et al. 1998, Tilman 2000). This idea of functional diversity and complementarity is beautifully illustrated by the work of Pate and Bell (1999) in the *Banksia* woodlands of Western Australia. By digging up entire trees and other dominant species in the landscape, Pate and his co-workers were able to show that there was as much underground structural and functional diversity as there was above ground. Furthermore there was a temporal component to the functional diversity whereby different species grew at different times of the year. In this way high water use efficiency was ensured at the community level.

Habitat fragmentation usually produces fragments of the original regional ecosystems in the landscape in which the species biodiversity is some linear fraction of the original biodiversity (Type I distributions, Gaston 2000). To a large degree the species complement of the fragments can be predicted by fragment size and by the physical habitat template. In other words such parameters as aspect, temperature, rainfall and the nutrient status of the underlying soils largely determine the composition of the fragment. This type of predictive framework has been confirmed for native Australian eucalypts by Austin (Austin 1998, 1999, Austin et al. 1996) who showed that the distribution of these trees could be largely predicted by a set of General Linear Models which combined a small number of important physical habitat attributes.

We now realise that catchment processes are one of the primary determinants of water quality (as well as in stream processes). As soils develop and age, and the biodiversity of the terrestrial vegetation develops, so also does water quality change over time. A recent paper by Engstrom et al. (2000) has demonstrated just how closely water quality is determined by the development of soils and vegetation in the catchment of a number of small glacial lakes in Alaska. This paper is the first documented temporal sequence (chronosequence) for water bodies spanning the last 10,000 years.

Thus we might reasonably expect that as catchments are cleared and land use is changed there will be a relationship between say, decreased forest cover, and the increased leakage of water and nutrients from the catchment. This will be reflected in the water quality of the stream or river draining that catchment (eg Williams and Melack 1997). Pristine forested catchments or those with their original cover of bush should leak little (although never zero because of climate perturbations and spatial patchiness, Harris 1999b). Reductions in forest cover and changes in soil type through fire or clearing should result in increased leakage and declining water quality (Talsma and Hallam 1982). As there are complex interactions between the species in the remaining habitat fragments and between the fragments and the surrounding agricultural and urban land use, we might expect these relationships to be non-linear.

One way to think of the movement of nutrients in catchments – which are made up of a mosaic of soils, land uses and of river reaches, wetlands and water impoundments – is to use Vollenweider's OECD (1968) formulation in terms of the factors that influence retention of nutrients (either C,N or P) in the reach, storage or wetland. Thus there is a simple theoretical basis for relating sources and sinks in the landscape and watercourse – and hence the varying water quality in the rivers. The fundamentals of this theory were laid out by Vollenweider (1975) and also by Ahlgren et al. (1988) and reviewed in the Australian context by Harris (1994). Movement of energy and materials downstream are controlled by the physiology of the component species (Harris 1999a,b)

Hysteresis effects in aquatic ecosystems.

What, then, is the response of the aquatic ecosystems to changing land use in the catchment? Harris (1997) proposed a simple modelling framework for aquatic ecosystems based on simple principles. The interactions within and between functional groups of organisms in ecosystems can be modelled and can be used to explain the overall responses to perturbation (Harris, 1997, 1998, Loreau 1998a). Harris (1999a) showed that by combining the known physiologies of the most important functional groups in aquatic ecosystems, such a conceptual framework could be used to explain the overall "physiology" of freshwater and coastal marine ecosystems. This was the basis of the model of Port Phillip Bay (Murray and Parslow 1999a,b), which was itself the basis of the management recommendations for the Bay (Harris et al. 1996).

Aquatic ecosystems exist in two states, either clear and macrophyte dominated or turbid and plankton dominated (Scheffer et al. 1993, Scheffer 1998). We know that lakes and estuaries show these responses – there is also anecdotal evidence that rivers are similar. The switch between the two states is often abrupt and the ecosystem response to perturbation is highly non-linear and complex. The non-linearity arises from the strong interactions between the pelagic and the benthos and competition between the two sub-systems for light and nutrients. Nevertheless the characteristic response shows strong hysteresis, that is when the ecosystem state shifts from one state to the other (eg clear to turbid) it is highly resistant to switching back. ie ecosystems can show "critical loads" (as Port Phillip Bay, Harris et al. 1996) or "points of no return" which are of great concern for managers. As Scheffer (1998) has shown, the observed water quality of the two states is quite different in terms of nutrients and turbidity. The “switch” from one state to the other is visible in the water quality data from these systems. The simple functional group models proposed by de Angelis (1992), Harris (1997, 1998, 1999c), Murray and Parslow (1999a,b) and others faithfully reproduce the observed non-linear behaviour and water quality changes of the natural ecosystems.

One thing, which is very clearly displayed by these simple models, is a very strong effect of changing the water residence time or the flushing rate of the system. Increasing the water flow (reducing the water residence time) washes out the pelagic organisms and so switches the interactions strongly in favour of the macrophytic plants and the benthos. Increasing the water residence time and reducing the flushing allows the plankton to grow and out compete the macrophytes and benthos. Systems that are highly flushed can be clear and dominated by aquatic macrophytes. Systems with long residence times tend to lose their macrophytes and be dominated by plankton. The models show that small changes in the flushing rates of rivers, lakes and estuaries have a major impact on the ecosystems and their water quality (Harris 1997, 1998, 1999a, c). Changes in water flows are at least as important as changes in land use when it comes to impacts on aquatic systems (Heggie and Skyring 1999). I shall return to these models and results later when I discuss the interpretation of the water quality data.

One result of the effects of varying water residence times is to change water quality downstream of reservoirs and wetlands. Anywhere where there is lengthy contact with the benthos or riparian vegetation leads to stripping of nitrogen through biological uptake or denitrification (Axler and Reuter 1996). Wetlands dominated by emergent and submerged vegetation have large surface areas of various biofilms that have been identified as the key sites of microbial activity (Risgaarpetersen and Jensen 1997). Similarly, Australian reservoirs are either monomictic (mixing once a year in late winter) or meromictic (mixing occasionally every few years) and are anoxic below 5-7 metres (Harris and Baxter 1996). The anoxic hypolimnia of reservoirs are regions of active microbial activity and most reservoirs appear to be sources of ammonia and nitrate (Straskraba 1998, 1999).

Water quality in rivers is therefore a function of land use and catchment geology as well as in-stream interactions, including position in the overall landscape pattern of regulated reaches, reservoirs and wetlands. Land use change in Australia has tended to increase flow regulation and the number of impoundments and weir pools of various kinds. Simultaneously the Australian continent is losing wetlands rapidly because of flow regulation and drainage. All these changes will alter river water quality and there is now a reasonable theoretical basis for our understanding.

Analysis of the water quality data – methods and data sources

The analyses of the data undertaken in this report are very simplistic. The water quality data quoted here are a combination of annual medians, annual flow-weighted means and other individual sample results. Wherever possible long-term means are used (often from hundreds of individual samples collected over periods as long as 25-30 years). The use of long-term station means is admittedly only a first cut at the data – there are more information in terms of the effects of individual storm events and long-term trends. This report must be viewed as the initial part of a long-term work in progress.

Analysis of the data from individual stations shows that they are quite regular in their statistical distributions and that cross plots of such parameters as total nitrogen (TN) and total phosphorus (TP) show regular relationships across a range of flow regimes (Fig 1). These station means are not normally distributed; indeed they approximate lognormal distributions and hence are generally presented as log-log plots (eg plots of TN vs TP). While, on account of the distribution of the data, it might have been preferable to use geometric means rather than arithmetic means. Arithmetic means have been used here because of their prevalent use in the literature and because there does not seem to be a large bias in their use (Elsenbeer et al. 1994). Others have commented on the variance structure of water quality data and on the necessity of log transformations to avoid undue leverage in regression by a few data points (see eg Harris 1987). The lognormal data distributions arise from the exponential nature of the underlying processes (growth and nutrient uptake) as well as a central limit phenomenon arising from the multiplicity of species involved (May 1974). In addition, water quality data from catchments is now known to reflect the fractal nature of catchment processes (Kirchner et al. 2000).

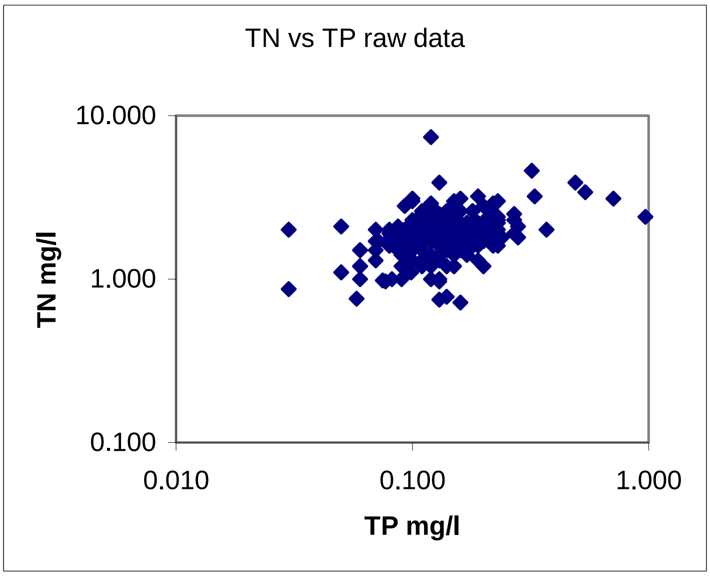


Figure 1: A scatter plot of raw data from the Swan River (WA Water and Rivers Commission data) showing that the data are regularly distributed and that means of N and P can be plotted.

Data were obtained from various "grey" literature sources. Each source is fully referenced in the text. Perhaps the most useful source of water quality is that to be found at www.vicwaterdata.net - a compilation of all the Victorian State water quality data for the past 25 years or so, placed on the web by a consortium of Victorian State Agencies (see also Cottingham et al. 1995). Many of the analyses discussed below are based on these data.

The methodological limitations of water quality data from the "grey" literature data must also be acknowledged. Some individual data points appear to be erroneous because of sampling and analytical errors, errors in compilation and reporting and unacceptably high detection limits. Many of these problems become obvious during analysis and as long as they are analysed with care, there is much useful information in summary statistics. (Some examples of data quality problems will be noted below.)

Most water quality reports did not contain the full suite of parameters required – both total nutrient concentrations (TN, TP) and the break down of the totals into dissolved organic N (as total Kjeldahl N, TKN); and dissolved inorganic N and P (DIN as nitrate and ammonia; and DIP as soluble, molybdate reactive, phosphate). Full analysis of the water quality data in State reports was therefore limited to those data sets containing the required data.

Essentially what was generated by the use of station means was a set of mean water quality statistics for a sample of river reaches in particular catchments or regions. Plots of water quality parameters were compared as stoichiometric relationships i.e. TN: TP or dissolved inorganic N (DIN) and DIP. These stoichiometric relationships were compared to the Redfield ratio (Redfield 1958) as a reference ratio. The Redfield ratio (106C:15N:1P by atoms) is the stoichiometry of C, N and P in living micro-biota (Harris 1999a) and is the ratio of these nutrients in the deep ocean. The Redfield ratio is used as a reference because of the ubiquitous role played by microorganisms in the cycling of elements in the biosphere (Ehrlich 1998, Harris 1999a).

Catchment exports were calculated, where possible (as tonnes N or P km^{-2} y^{-1} or kg N or P ha^{1} y^{-1}), by combining water quality and hydrology data, together with data on the catchment area contributing to a particular station. Raw data for the State of Victoria were obtained from the web site and from the Victorian department of Natural Resources and

Environment. Grayson et al. (1997) used similar data from the Latrobe River in Victoria to obtain a “snapshot” of catchment influences and water quality.

Because of the obvious problems in using annual means for both flows and water quality data (many data sets are biased by a small number of large flow events) flow weighted data were employed where possible. Flow weighted export data are, however, rare in the Australian context. Swistock et al. (1997) analysed the errors associated with the use of various sampling regimes.

Relationships between land use, hydrology, catchment exports and water quality

By searching the international and the “grey” literature for reports containing basic water quality information and land use, it was possible to assemble data sets for a series of catchments where various components of surface water quality were related to forest or other forms of plant cover.

In a series of plot experiments McIvor et al. (1995) examined the relationship between plant cover and surface run off. During large rainfall events there was little or no relationship – at high rainfall intensities plant cover has little impact on the hydrological balance. For medium to low rainfall events however McIvor et al. (1995) found the expected non-linear relationship between plant cover and run off. Below about 50% cover run off increased sharply. Similarly, in the same experiments, sediment concentrations in the run off water also increased non-linearly as plant cover was reduced. Stream power is related to slope and rainfall intensity so that once slopes are cleared then the surface run off has sufficient power to begin to cut down into the soil and subsoil (Prosser et al. 2001, and references therein). Gullying and erosion produces high total suspended solids (TSS) concentrations in rivers and streams. The TSS loads are composed of a wide range of size fractions – from fine clays to quite large pebbles and rocks. The coarser eroded material (particularly the sand fraction) is transported downstream and stored in the middle reaches of the catchments where slope and water velocity decrease (Wasson et al. 1996). Suspended clays may have very low settling velocities (particularly in sodium dominated waters) and will be carried far downstream. These waters with high TSS and suspended clay loads are very turbid and light penetration is poor.

As plant cover is reduced water begins to move more rapidly down slope and across the landscape. Similarly recharge increases as plant cover is reduced because of the less efficient use of soil moisture. Wood (1924) made the first observations of this type in Western Australia. In a study of some catchments around Canberra, Walker et al. (1998) found a similarly non-linear relationship between forest cover and the conductivity and salinity of streams draining these catchments. Again, as forest cover is reduced stream conductivity increased and the cut off point separating the high and low conductivity regimes was around 50% forest cover. Sharma et al. (1980) had noted a similar effect in Western Australia. They observed a significant increase in salinity in creeks draining catchments that were more than 30% cleared. These data illustrated the increased impact of saline ground waters on stream flows as forest cover was reduced. Ground water influences on water quality were clearly higher in cleared catchments. Salinity of streams draining catchments is a good integrator of many processes associated with land clearance – notably movement of ground water and the mobilisation of salt stored in the soil profile.

Land use and population density also influence exports of nutrients to streams within catchments. Gerritse and Adeney (1992) found that nutrient concentrations in streams draining sub-catchments in the Stirling Ranges near Perth were a function of the proportion of orchards in the catchments and also a function of urban development. Gerritse and Adeney (1992) showed that nitrate concentrations in the streams were a function of fertiliser use in the orchards in the catchments. In the Sydney region careful studies by Simeoni et al. (1994) and Ferguson et al. (1995) showed a strong impact of land use and urbanisation on nutrient exports from catchments. I shall discuss these data in more detail below.

Analyses of major ion data

Williams and others published the definitive early work on the major ion chemistry of Australian waters more than 30 years ago (eg Bayly 1964, Williams 1967, Douglas 1968, Bayly and Williams 1973, Johnson and Muir 1977, Muir and Johnson 1979). As expected a clear link between the underlying geology and water chemistry was discovered.

Surprisingly, this early work in catchment biogeochemistry was carried on not in the limnological or the aquatic ecology community, but by the foresters who were interested in the fertility and sustainability of forested catchments (see Attiwill et al. 1978, Guthrie et al. 1979, Flinn et al. 1979, and more recently Crockford and Richardson 1998). Little work has been done since, exceptions being Banens (1987), the more recent work of Elsenbeer et al. (1994), Hayes and Buckney (1995), and Markich and Brown (1998) in the Hawkesbury Nepean. Some work has been done on the impact of forest fires on water chemistry (Mackay and Robinson 1987). All in all, little use has been made of the major ion chemistry data in recent years.

Using data from more than 80 stations in the State of Victoria where a wide range of water quality parameters were collected for periods up to nearly 30 years, I assembled a set of data on major ion composition in these waters. Plotting a Gibbs diagram for the Victorian data (Fig 2) gave a not unexpected result. Victorian surface waters were more sodium dominated than world average fresh waters (wafw) – a result of long term leaching and weathering in the landscape. Also many surface waters showed a remarkably sea water (sw) like composition, a result of the mobilisation of cyclic sea salts from the soil profile (Herczeg et al. 2000) following increased recharge, ground water rise and discharge into surface waters. The State of Victoria is a model State in many respects, with surface water quality and discharge being highest in the eastern catchments where forest cover is still widespread. Water quality declines towards the west as land clearing becomes more prevalent and agriculture more widespread. The saline surface waters occurred frequently in the western part of the State.

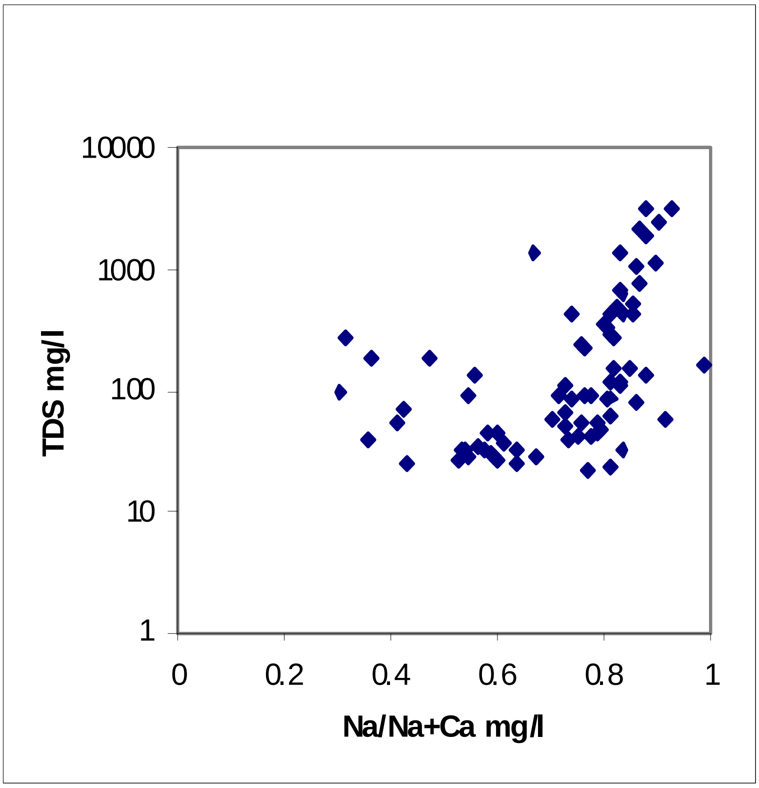


Figure 2: A Gibbs plot of major ion data from 84 stream sampling stations in Victoria. Data from www.vicwaterdata.net. wafc: world average freshwater composition. Sw: seawater composition. Victorian surface waters are generally sodic (sodium dominated) and many have a remarkably seawater like composition, reflecting the influence of saline ground waters.

The Victorian data showed strong correlations between total organic carbon (TOC) and sodium, and between calcium and sulphate (Fig 3). Thus there was much more than just salinity (sodium and chloride) moving down these catchments. Indeed the signature began to look very like the signature of strongly acidic and sodic soils. Chartres and Geeves (1992), Chartres et al. (1990) and Helyar and Porter (1989) discussed the chemistry and distribution of acidic soils (which are much more widespread than saline soils). Soil acidity became more widespread as a result of the introduction of subterranean clover in the early 1950s. Cox and Ashley (2000) showed sodic water quality signatures draining small catchments in the Adelaide Hills where Naidu et al. (1993) and others have studied the drainage water from the acidic and sodic soils.

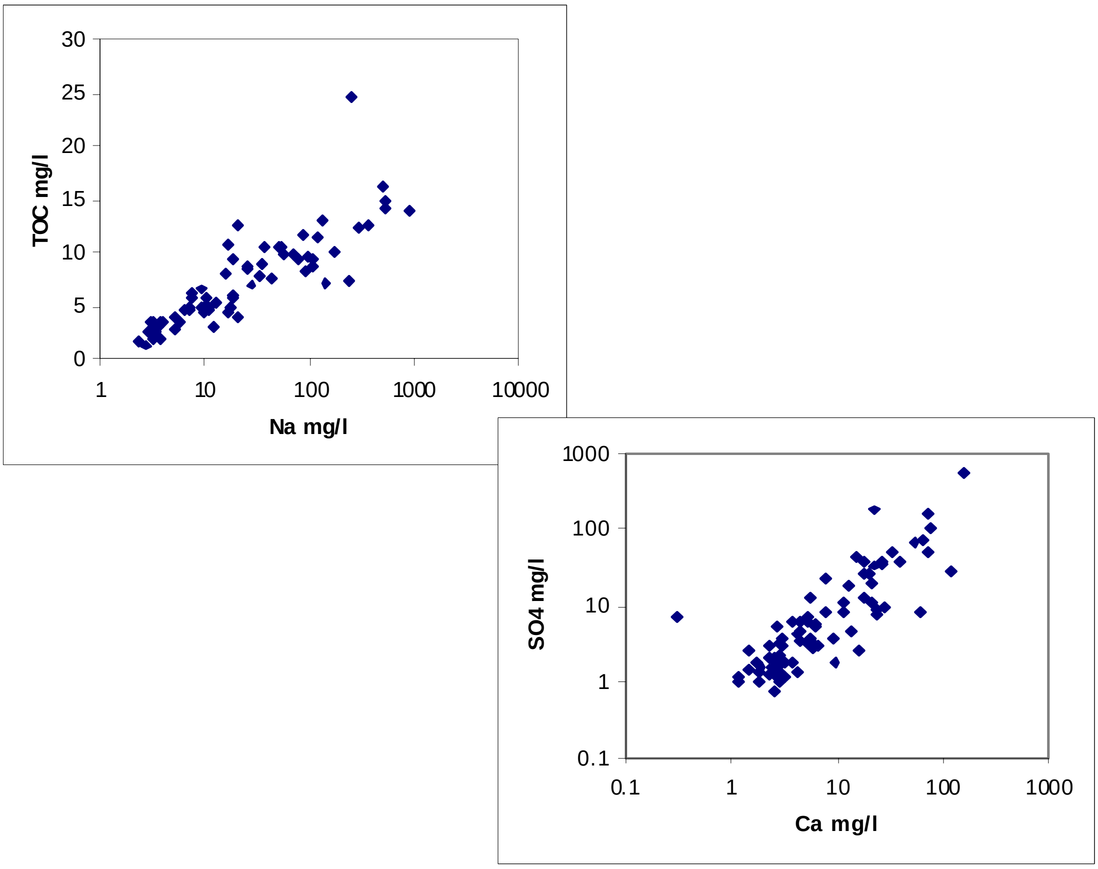


Figure 3: Victorian water quality data: correlations between water quality parameters in the subset of 84 stations with full water quality data.

Further analyses of the Victorian data (Fig 4) showed evidence of correlations between TOC and iron, between iron and TP and between nitrate and sulphate and iron. Similar relationships are known in sediments (Gerritse 1999). Colloidal forms of carbon and complexes with humic acids of various kinds control the chemistry in these waters (Viers et al. 1997). These analyses revealed a number of expected relationships in waters of increased conductivity and salinity draining acidic and sodic soils – work largely done in South Australia (Naidu et al. 1993). The soil science literature documents the effects of soil sodicity on the composition of through flow (Naidu et al. 1993) and broader environmental impacts (Sumner et al. 1998). These soils break down easily and the water draining them contains high total suspended solids (TSS) concentrations. Much dispersed clay remains in suspension because the water is low in divalent cations. Also the water is high in TOC and iron (Fitzpatrick et al.1996, Nelson et al. (1996), Fleming and Cox, (1998), Hollingsworth and Fitzpatrick (personal communication), Cox et al. (1999), Cox and Ashley 2000). TP is correlated with the iron because much of the P is in the form of insoluble iron-P complexes. As expected the dissolved inorganic phosphate (DIP) concentration decreases as the iron increases. In most cases the DIP is about 15-35% of the TP (Fig 4).

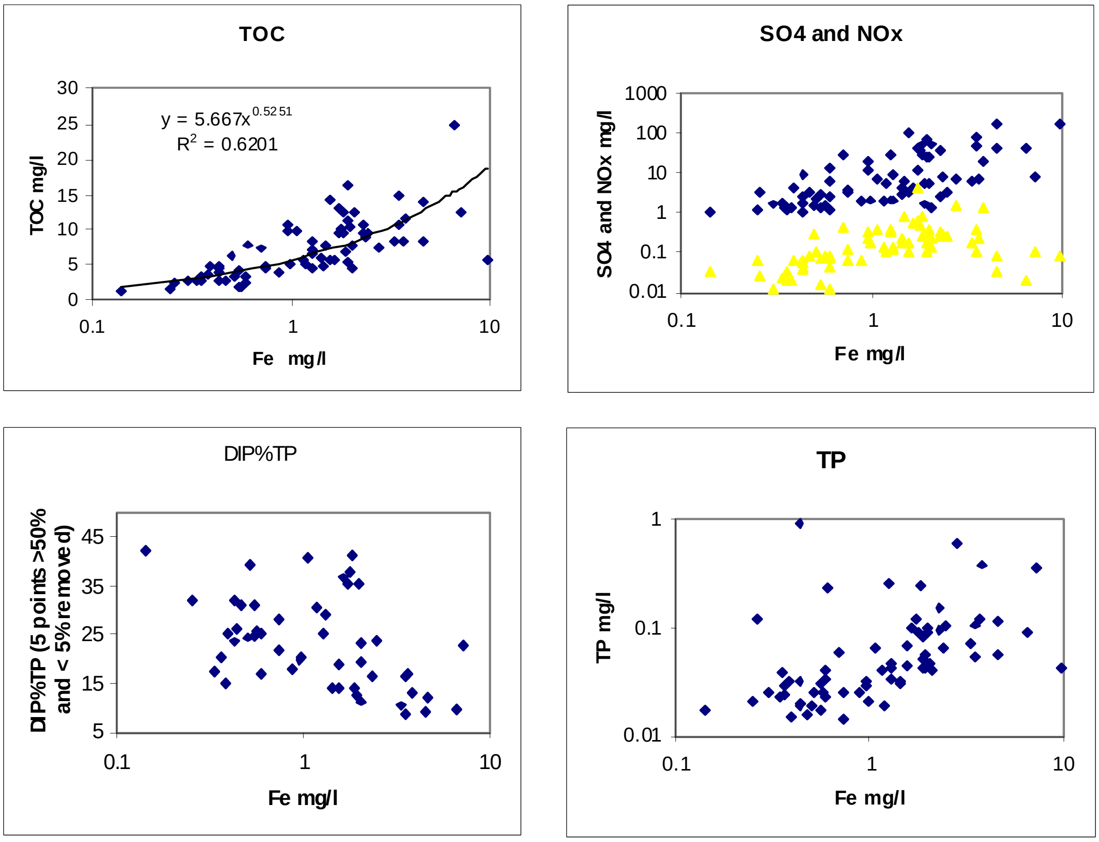


Figure 4: Victorian water quality data: correlations between iron and other major ions.

High levels of sulphate and nitrate in these waters indicate the generation of acidity and also the possible oxidation of pyrite in these catchments (Fitzpatrick et al. 1996, Cox et al. 1999). The surface waters have the characteristics of those draining acidic and sodic soils. Most Australian soils are poorly buffered and tend to be made acidic by the clearing of the land and the cultivation of crops like legumes – which are nitrogen fixers and generate nitrate in the soil profile. Many of these Australian major ion signatures in rivers are reminiscent of the results of acid deposition in the northern hemisphere. While we in Australia do not suffer from widespread deposition of sulphate and nitrate from the atmosphere (Holland et al. 1997), acid generation in soils has similar effects. Calcium leaching is associated with acid deposition (Likens et al. 1998) and acidity alters the chemistry of both ground waters and surface waters (Cosby et al. 1995, Jenkins et al. 1997, Smart et al. 1998).

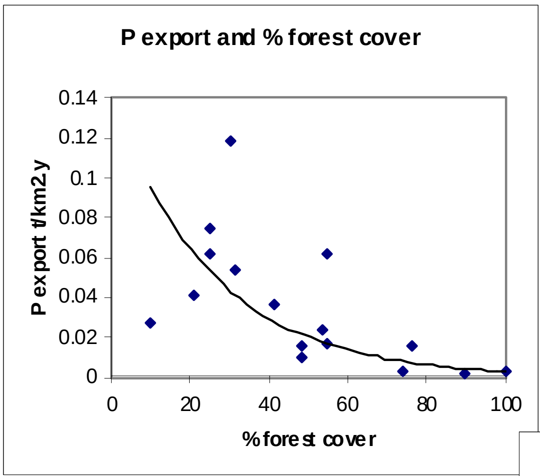
Donnelly et al. (1997) observed some important interactions between turbid, sodic waters with high TSS concentrations (where photosynthesis is reduced because of the high turbidity) and saline intrusions with high sulphate concentrations. Introduction of high sulphate waters into the Darling River in 1991 led to flocculation and setting of the clays, improvement in the underwater light climate. Also P was released from bottom sediments as a result of the interactions between iron, sulphur and phosphorus (Roden and Edmonds 1997). A massive algal bloom resulted. A knowledge of the interactions between carbon, sulphur, iron and phosphorus (Fig 4) is critical to an understanding of the impact of altering land use on Australian rivers and estuaries (Donnelly, et al. 1997, Gerritse 1999, Harris 1999a, Kleeberg 1998)

Thus the Victorian surface water chemistry clearly showed the impact of land degradation in the composition of its major ions. The next task is to look into the time course of these chemical processes and to look in more detail at the spatial relationships between soil types, cropping practices and water quality. The search for indicator measures in these waters indicated that salinity (as EC units) was highly correlated with the major ion chemistry of the water – notably Na^+ and Cl^-, although Ca^{++} and SO_4^{--} played lesser roles. Correlation coefficients of $R^2 > 0.95$ between EC and major ions were found in the Victorian data. Salinity is therefore a good indicator of perturbed major ion chemistry and, because the movement of ground water through the soil profile is a good integrator of many results of land clearance and agricultural development (Fig 4), water salinity is a good integrative indicator. Water salinity was not, however, a good predictor of other biologically relevant indicators of water quality (eg N and P).

Nutrient exports from catchments with varying land use.

Using a combination of data on water quality, hydrology and contributing area in the catchment allows the calculation of areal catchment exports of such things as TN and TP. This has been widely practiced overseas (eg Caraco 1995, Caraco and Cole 1999, Carpenter et al. 1998, Downing et al. 1999, Howarth 1998, Howarth et al. 1996, Kroeze and Seitzinger 1998, Lewis et al. 1999, Nixon et al. 1996, Seitzinger and Kroeze 1998) but less commonly done here in Australia (Young et al. 1996, Harris 2000). The available evidence has tended to indicate that nutrient exports from Australian catchments are lower than those from European and North American catchments (Caraco 1995, Young et al. 1996). The reasons for this appear to lie in lower rainfall and runoff, flatter topography, lower fertiliser use and lower population densities on this continent.

Perhaps the most complete set of analyses is that of Weaver and Prout (1993), Weaver et al. (1994, 1996), Weaver and Reed (1998) in the catchments surrounding Albany WA, and the data in Eyre, Pepperell and Davies (1999) from tropical Queensland (Fig 5). As with the run off, salinity and TSS data the response to decreased forest cover was shown to be non-linear with exports of TP rising sharply below 50% forest cover. Bott (1993) documented a similar relationship for the effects of broad-scale agriculture in Western Australia. Clearly, ecosystem function is severely compromised with this degree of fragmentation.



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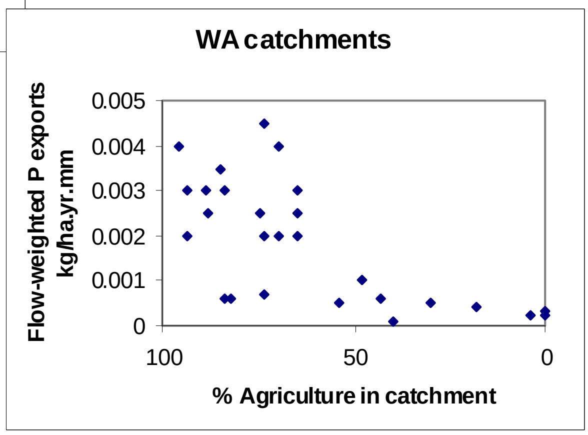


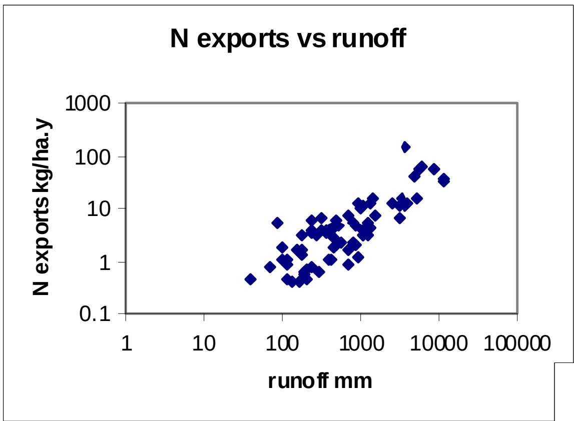
b

Figure 5: Phosphorus exports from Australian catchments. (a) Queensland data from Eyre et al. (1999) and (b) Western Australia data from Bott (1993).

There are a variety of data sources in Australia that have not been analysed from the point of view of comparative catchment biogeochemistry. There are data for 24 Sydney catchments in Simeoni et al. (1995) and Ferguson et al. (1995) – these have been analysed in Harris (2000).

As with the WA and tropical Qld data, exports of TN and TP from NSW catchments rose sharply as catchments were cleared and population densities in the catchments rose. By world standards exports from relatively pristine catchments were low, reflecting the generally low population densities and low fertiliser use compared to the northern hemisphere.

TN exports from Australian catchments were found to be lower than those from northern hemisphere catchments for two additional reasons. First, there is heavy atmospheric deposition of nitrate in the rain in the northern hemisphere. This source of acid rain is small to insignificant in Australia, the only major continent where this was found to be so (Holland et al. 1997). Second, in all cases so far studied TN export is strongly correlated to run off. This was found to be the case in the Victorian data, for example (Fig 6). Because the Australian run off is lower than just about any other continent TN exports were also found to be lower. TP exports are also related to runoff both in Victoria (Fig 6) and in Western Australia (Bott 1993). Australian TP exports are also lower than most other continents for the same reasons as TN exports – lower runoff, lower fertiliser use and lower population densities (Caraco 1995). The variability around the runoff relationship is related to catchment specific interactions between the land use and its connection to the watercourse. This is related to catchment topography and ground water dynamics (Creed and Band 1998).



Victorian catchment data

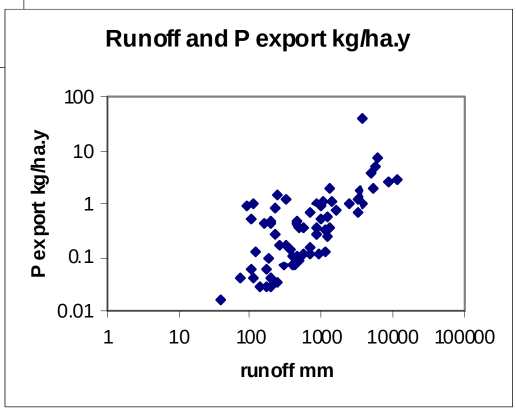


Figure 6: TN and TP exports as a function of runoff. Data on water quality and hydrology from www.vicwaterdata.net and catchment area data from Victorian Department of Natural Resources and Environment files.

What Harris (2000) discovered in his analyses of both the NSW and Victorian data was that as TN exports increased the form of the N changed from predominantly dissolved organic N (DON) to dissolved inorganic N (DIN – nitrate and ammonia). The data in Simeoni et al. (1995) and Ferguson et al. (1995) showed this effect very clearly (Harris 2000). Thus calculation of the proportion of TN that was DIN in the exports and plotting this versus TN exports showed a clear rising trend (Harris 2000). Dissolved inorganic P (Soluble reactive P or molybdate reactive P, DIP) was an almost constant fraction of the TP leaving the NSW catchments.

While a number of cases of TN, TP, DIN and DIP exports could be found in the "grey" literature or could be calculated, there were, regrettably, very few good data sets for carbon exports from Australian catchments. As far as is presently known from catchments around the world, total organic carbon (TOC) exports are largely independent of land use, and are more dependent on the soil C:N ratios under different ecosystems (Aitkenhead and McDowell 2000). Fortunately some of the Victorian data sets were found to have sufficient TOC data to be able to calculate TOC, TN and TP exports. These relationships were plotted (Fig 7).

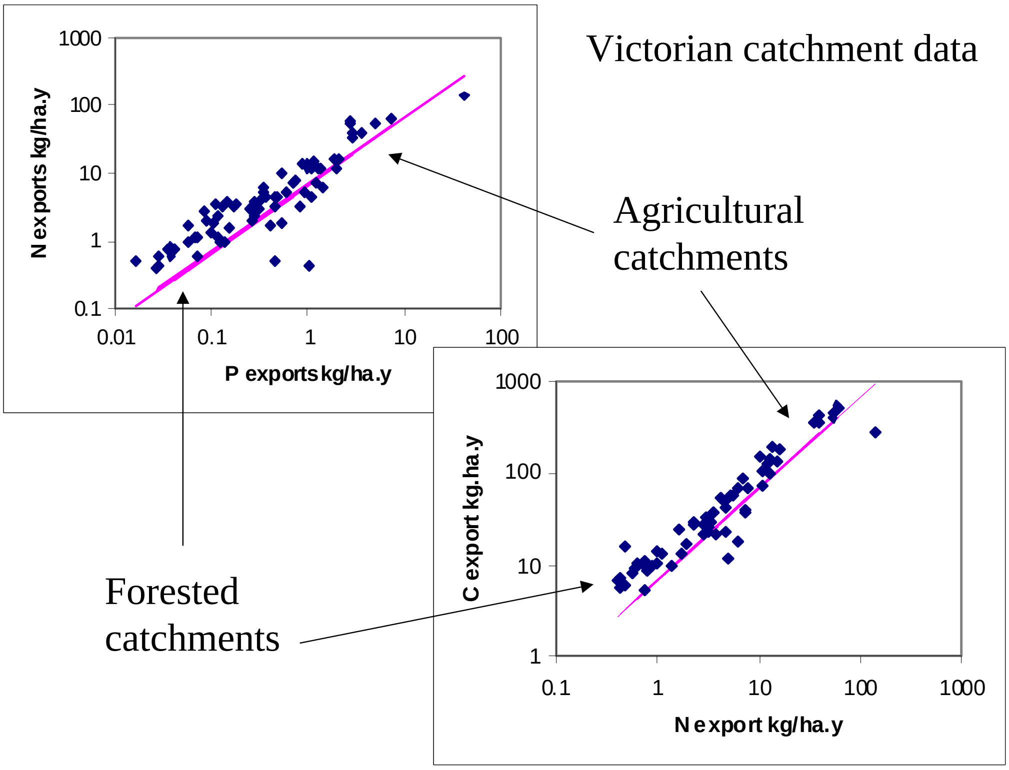


Figure 7: N:P and C:N ratios in catchment exports from Victorian catchments. Data calculated as in Fig 15. Forested catchments show higher C:N and N:P due to exports of DON.

Both C:N and N:P ratios were somewhat above the reference Redfield ratio line (Redfield 1958). The Redfield ratio (the composition of microbial biomass, usually 106C:15N:1P by atoms) translates to C:N and N:P ratios of about 7 by weight. The Victorian TOC data were compared to the Total Kjeldahl N (TKN – equivalent to TON plus ammonia) data from the same stations and a strong correlation with a mean ratio of 12.6 (by weight) was obtained ($R^2 = 0.77$ N=74). Thus the mean C:N ratio of the organic material in the rivers had a weight ratio of slightly less than twice the Redfield ratio. This compares to a weight ratio of about 15 in surface soils (Clarke and Russell 1977). C:N export ratios were similar ranging from 10-20 by weight. N:P export ratios were also somewhat above Redfield ratios (Fig 7) with a tendency for the ratios to decline as the exports increased. This is consistent with a decline in the DON and an increase in the DIN fraction as discussed above. As noted above the absolute export rates for C, N and P were found to be lower that observed in most world rivers and catchments for the reasons noted above.

In-stream water quality data – local and regional patterns in coastal catchments

As observed above, when the N loading to the catchment from atmospheric or anthropogenic sources exceeded the ability of the trees and crops to take up the N then DIN exports from the catchment rose sharply. By analogy the same kinds of responses can be expected for both aquatic and terrestrial ecosystems. The aquatic ecosystem model discussed in the introduction (and shown diagrammatically in Fig 8) reproduced the same responses as observed in the catchments feeding the river reaches sampled. The model reproduced the change in the catchment loading ratios of TKN and DIN. If loads of N were slowly increased in a model of this kind, the proportion of the TN (the sum of the entire N in dissolved and particulate, living and detrital pools) that was DIN increased when the growth rates of the predominant primary producers were saturated. Indeed it has been shown theoretically that as the rate of N addition exceeds mP/2 (where m is the maximum growth rate of the primary producers, P) then the concentration of DIN will start to rise (Murray and Parslow 1999a, b). This means, in effect, that [DIN], the concentration of DIN in the water, will start to rise sharply once [DIN] = K_s the half saturation concentration of DIN uptake for the primary producers. The properties of the ecosystem response are therefore determined by a simple piece of basic physiology. Exceedences of ANZECC water quality parameters are more likely to occur once the uptake capacity of the in stream biota has been saturated by the catchment load. Because the location of the uptake and saturation processes of N and P differ – N largely littoral and P largely pelagic (Harris 1999a), then we can reasonably expect to see somewhat different patterns of N and P exceedences on occasion.

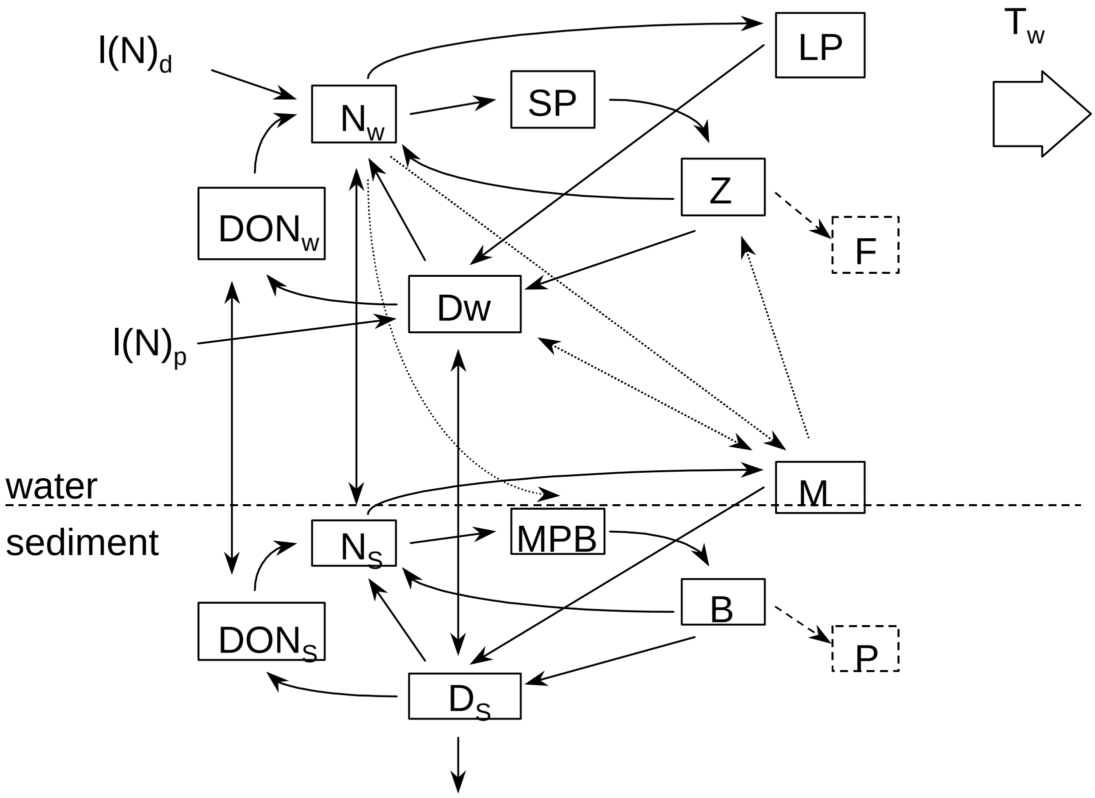


Figure 8: The schematic coupled model of pelagic and benthic processes in rivers, lakes and estuaries published by Harris (1997, 1998, 1999c) and the basis of the Port Phillip bay model of Murray and Parslow (1999a,b). N: dissolved inorganic nutrients in water and sediments, DON: dissolved organic nutrients in water and sediments, Dw and Ds: detritus in water and sediment, SP and LP: small and large phytoplankton, Z: zooplankton, F: fish, MPB: microphytobenthos, B: benthic feeders, M: macrophytic plants, P: predators on the benthic feeders.

DIN losses by denitrification require long water residence times and strong coupling between the sediment or the littoral vegetation and the water column (Axler and Reuter 1996) so are favoured by weir pools or impoundments with long water residence times (Fig 9) or those dominated by aquatic macrophytes. It has also been shown in work from the northern hemisphere that rates of denitrification were proportional to the DIN load (Fig 10 and Windolf et al. 1996). Thus we might reasonably expect to see DIN removal in slowly flowing, or impounded, river reaches and little elsewhere.

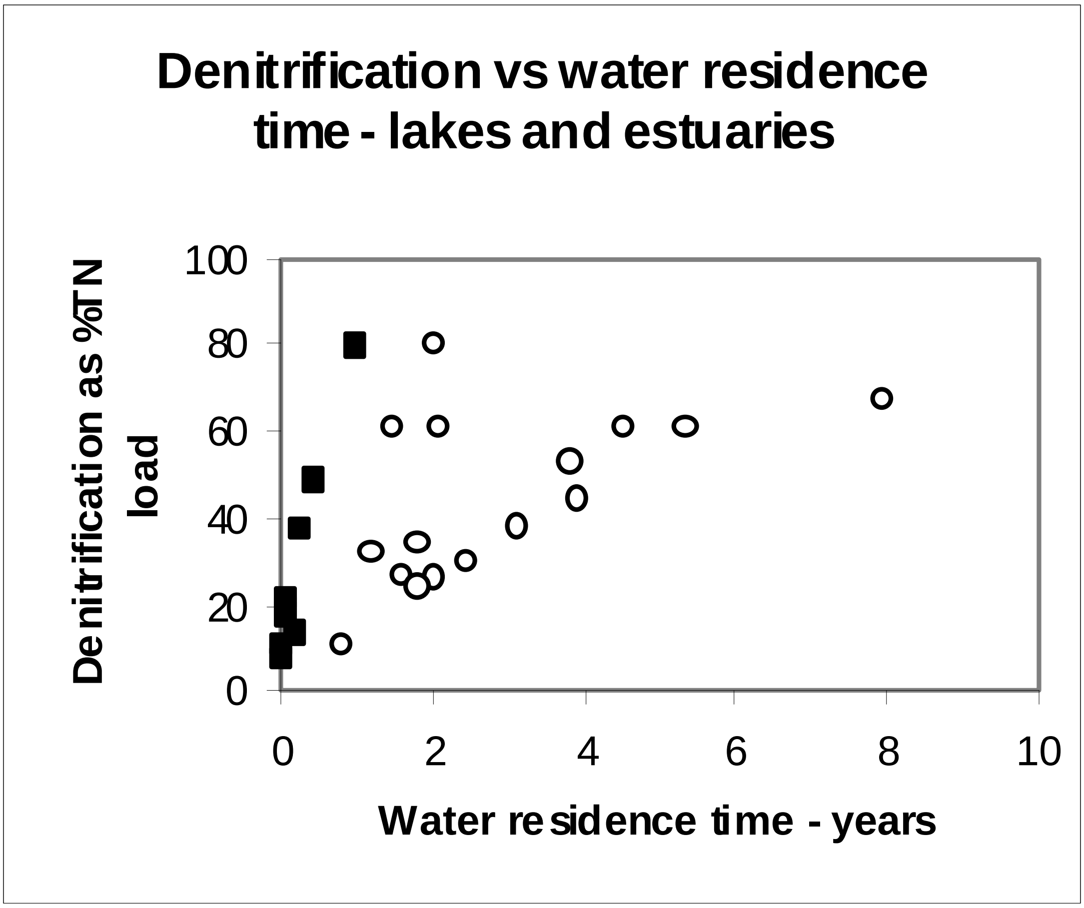


Figure 9: The relationship of water residence time to denitrification efficiency. Open circles, lakes. Lake data from Ahlgren et al. (1994), Molot and Dillon (1993), Vollenweider (1968), Closed squares, estuaries. Estuarine data from Seitzinger (1987, 1988).

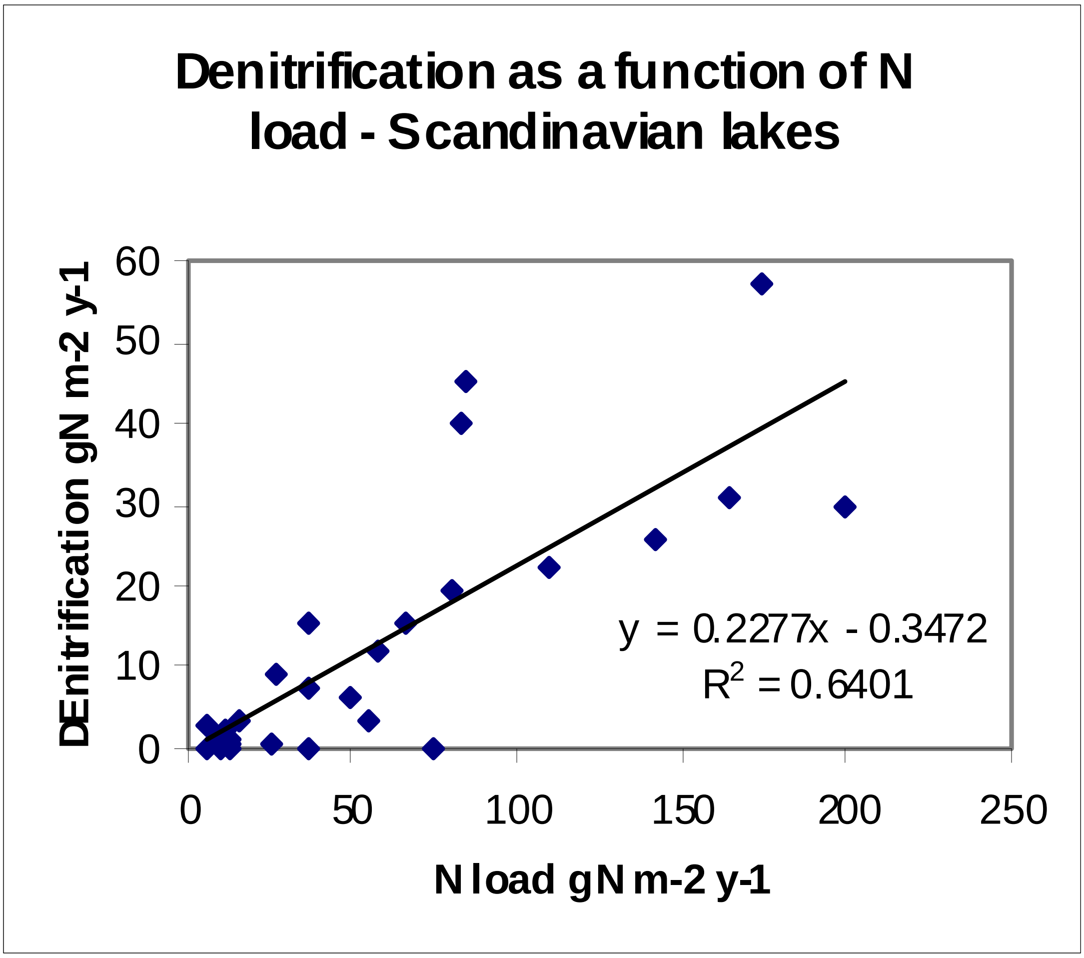


Figure 10: The relationship between N load and denitrification efficiency for a series of Scandinavian lakes. Data from Andersen (1974), Dudel and Kohl (1992), Gibson et al. (1992), Jensen and Dahl-Madsen (1978), Jensen et al. (1990, 1992), Messer and Brezonik (1978), Serruya (1975).

I have already discussed the effects on DIP concentrations of high TSS and TOC loads as well as high concentrations of Fe and other cations in water draining sodic and acidic soils. Thus interpretation of the stoichiometric plots for N and P was aided by knowledge of catchment land use, inputs, flow regulation and in-stream processing of the various forms of these elements.

1. Magela Creek in Kakadu National Park, NT

I begin with a data set from Magela Creek in Kakadu National Park in the Northern Territory (Figs, 21, 22, 23). Walker and Tyler (1982) published the data. These data illustrated some of the data analysis techniques to be followed with other, later, data sets. For other data from the

Magela Creek and floodplain see Hart and McGregor (1980), Hart et al. (1987a,b). Unfortunately Hart’s work does not record all the necessary forms of N. The data quoted in print lacks data for DON.

Data from Magela Creek were first plotted in the form of TN vs TP plots (using station averages, Fig 11). Dilute waters from the wet season showed TN:TP ratios above the Redfield reference line, and plots of TKN vs TP indicated, as expected, that in this mostly pristine catchment the N in these waters was predominantly DON. As the waters became richer during the dry season (and the waters become confined to billabongs) the concentrations of N and P increased and the line trended towards the Redfield reference line, reflecting more microbial processing and more interaction of the waters with the bottom sediments. Dilute waters reflected the dominance of catchment inflows, and the more concentrated waters of the billabongs reflected more benthic interactions and “in stream” processing.

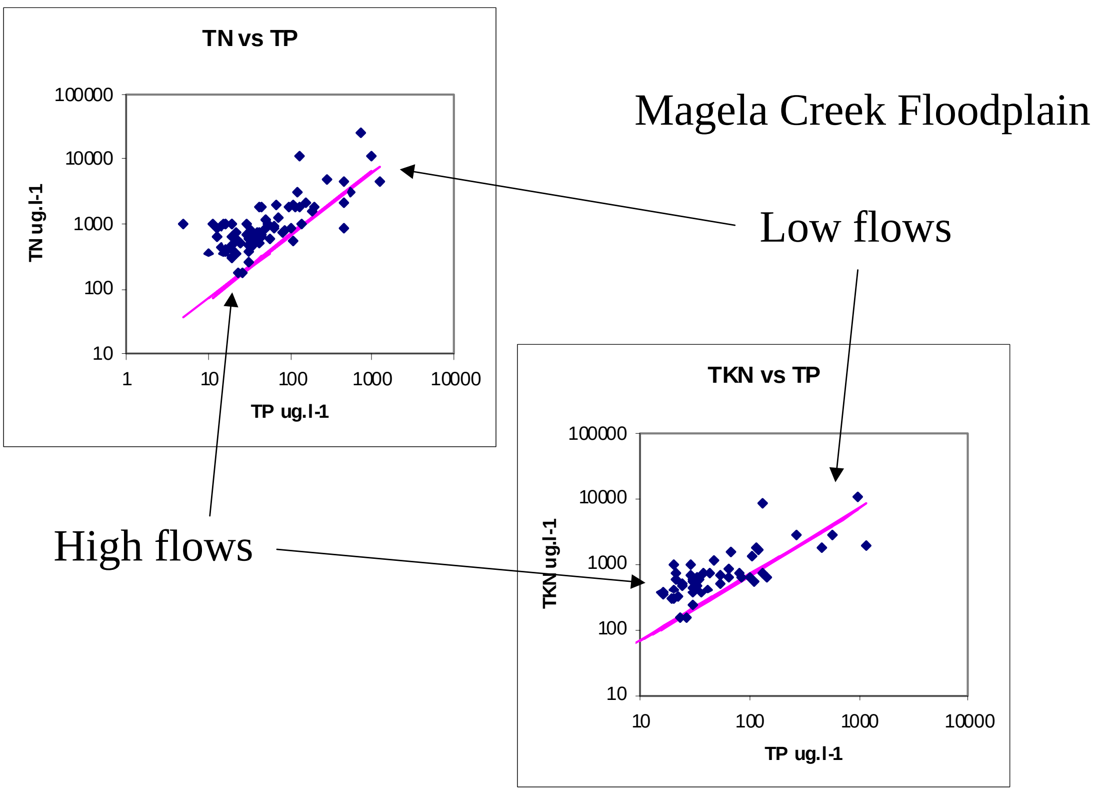


Figure 11: Magela Creek, NT – water quality data from Walker and Tyler (1982). In these and all subsequent plots the thin diagonal line is the Redfield ratio line for reference.

Plots of DIN vs DIP and DIN vs TP from Magela Creek (Fig 12), showed that while the TN:TP ratios were above Redfield, the DIN:DIP ratios were well below Redfield ratios in the dilute waters. This also reflected the predominance of DON over DIN in the run off from pristine catchments on this continent, driven by the high C:N ratios of the terrestrial vegetation and proportionally high TOC exports. Either denitrification in the catchment or low N inputs from N fixation would have led to the low DIN in these waters.

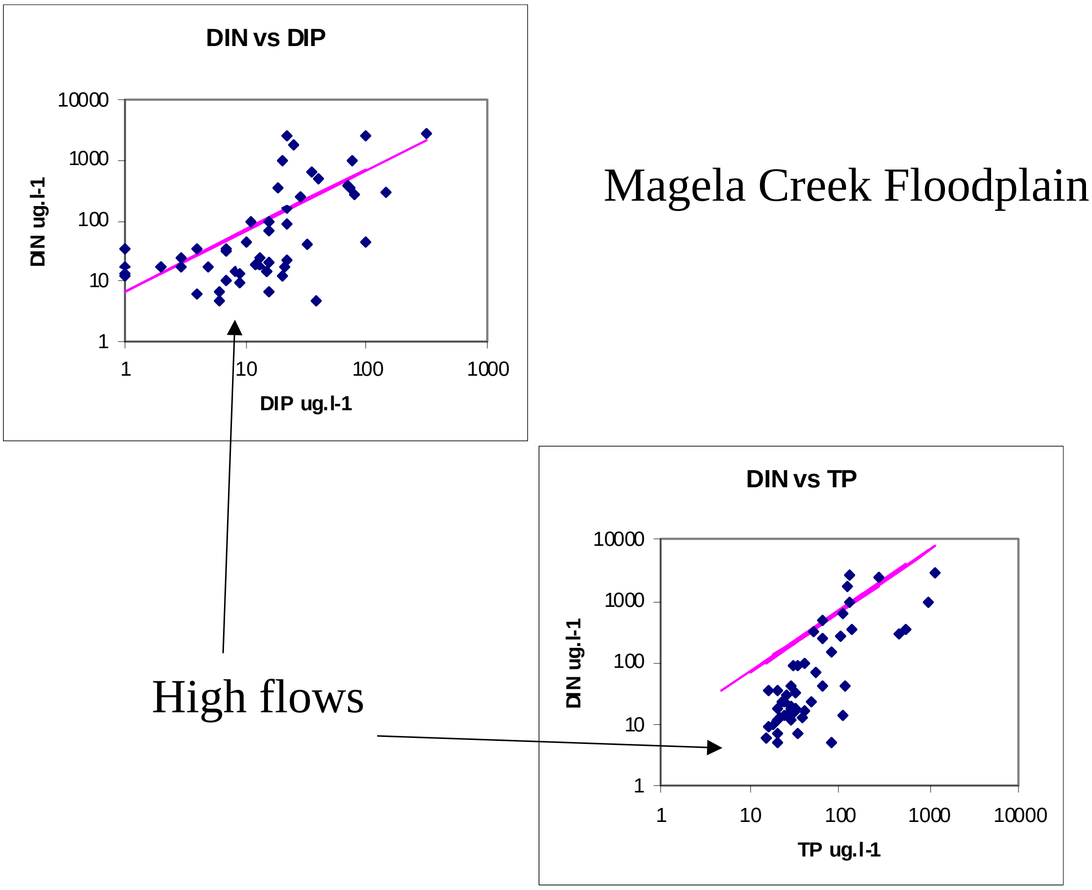
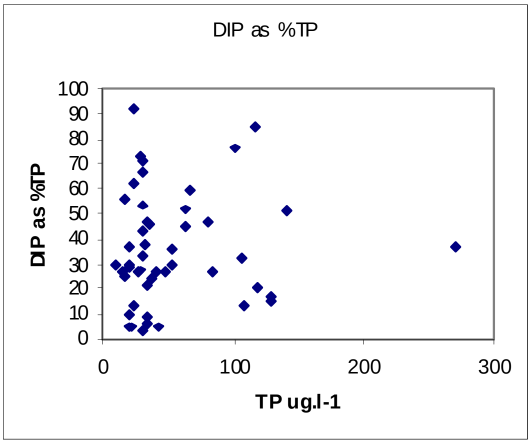


Figure 12: Magela Creek, NT – water quality data from Walker and Tyler (1982). The thin diagonal line is the Redfield ratio line for reference.

There is some reason to doubt the validity of the very low DIP data from Magela Creek. 1 ug/l was probably below the analytical capacity of the technique used (usually around 2 ug/l with the best techniques), so probably represented attribution to an arbitrary value below detection limits. Any plot of this kind showing lines of points at the detection limit of DIN or DIP (eg Fig 16) was suspect for the same reason. Plotting DIN vs TP showed a clear trend of widely ranging DIN values and low variability in the TP data (Fig 12). These data were therefore found to be consistent with the overall expected patterns of catchment exports from pristine catchments. Plots of DIN as %TN and DIP as %TP (Fig 13) showed little pattern in this case, other than the expected result of generally low DIN as %TN in these waters from forested catchments.



Magela Creek Floodplain

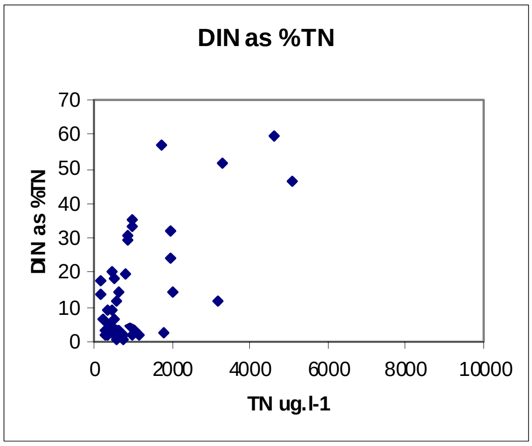


Figure 13: Magela Creek, NT – water quality data from Walker and Tyler (1982). The thin diagonal line is the Redfield ratio line for reference.

These data showed (somewhat surprisingly) that as flows varied seasonally the stoichiometry of N and P varied in a regular manner. The most dilute waters (lowest N and P concentrations) reflected the concentrations and stoichiometry of nutrients washing off the catchment at high flows. The highest concentrations of N and P were found in residual billabongs during the dry season and represented the water quality found in standing water after lengthy interactions with the sediments (Walker and Tyler 1982). The data showed a regular shift in concentration and stoichiometry from one extreme to the other (Fig 11). High N:P ratios at high flows were dominated by TKN washing off from the catchment – DIN concentrations were low (Fig 12), whereas the higher concentrations of N and P in billabongs were dominated by DIN and DIP.

2. Western Australian Rivers

The N and P data from WA rivers showed a number of different patterns. Malcolm Robb, Waters and Rivers Commission supplied raw data, but see also Swan River Trust (2000). Plots of TN vs TP again frequently showed high TN:TP ratios in the more dilute waters. Data from the Swan River in particular also showed high DIN:DIP ratios (Fig 14) – a lot higher than would have been expected from Redfield proportions. This could only be explained as an effect of land clearing and agricultural development in large areas of the catchment on N exports as nitrate. The very high DIP values in these data came from stations in Ellen Brook, an area of where the DIP was known to originate from septic tank effluent and DIP mobility in sandy soils was known to be high (Gerritse et al. 1998).

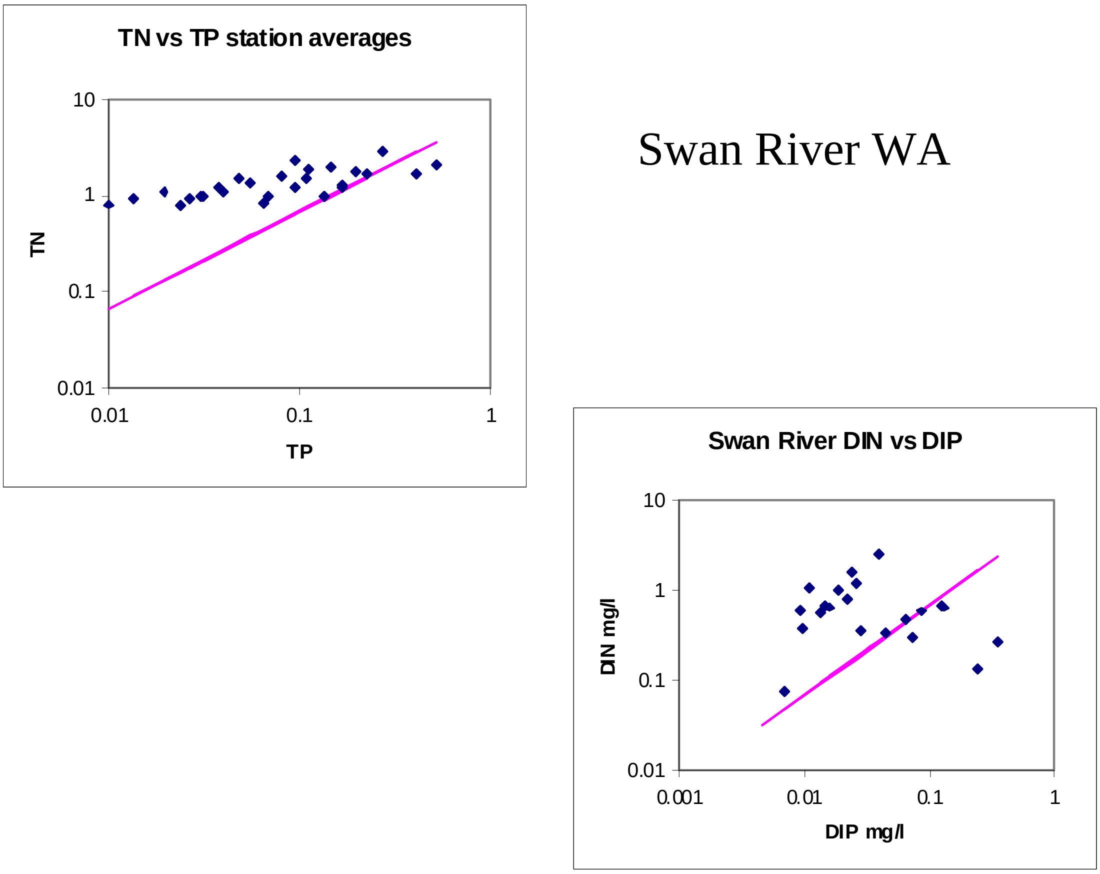


Figure 14: Water quality data from the Swan River, Wa. Data from WRC files courtesy of Malcolm Robb. (see Fig 1.) These data show high N:P and DIN:DIP ratios in the more dilute waters. The thin diagonal line is the Redfield ratio line for reference.

The relationships between TN:TP and TKN:TP were interpretable in the light of Victorian data – this was the only data set with sufficient TOC data to be able to explore relationships between C, N and P (see above). The Victorian data showed a very strong correlation between TOC and N as TKN. Thus it was reasonable to assume that the high TKN:TP ratios in the more dilute waters of the Swan River was a reflection of the high C:N ratios of the dissolved organic carbon and nitrogen (DOC and DON) sources in the catchment. Aitkenhead and McDowell (2000) showed that catchment DOC exports were a direct function of the C:N ratio of the source material. High C:N ratios were, in all probability, also responsible for the high TKN values found in these waters.

Water quality data from other WA rivers showed a mixture of responses to changes in land use and iron status in the soils (Jakowyna et al. 1999, South Coast Estuaries Project 1991a,b, Weaver et al. 1994, 1996, Weaver and Prout 1996, Weaver and Reed 1998). The most complete data sets were collected from catchments around Albany and Oyster Harbour (South Coast Estuaries project 1991a,b). Like the Swan River all these rivers tended to show high TN:TP ratios in the more dilute waters – tending towards the Redfield ratio at higher concentrations (Fig 15). The real differentiation between the rivers lay in their DIN and DIP data (Fig 16) and the way the DIN and DIP concentrations were determined by the proportions of TN and TP that were DIN and DIP.

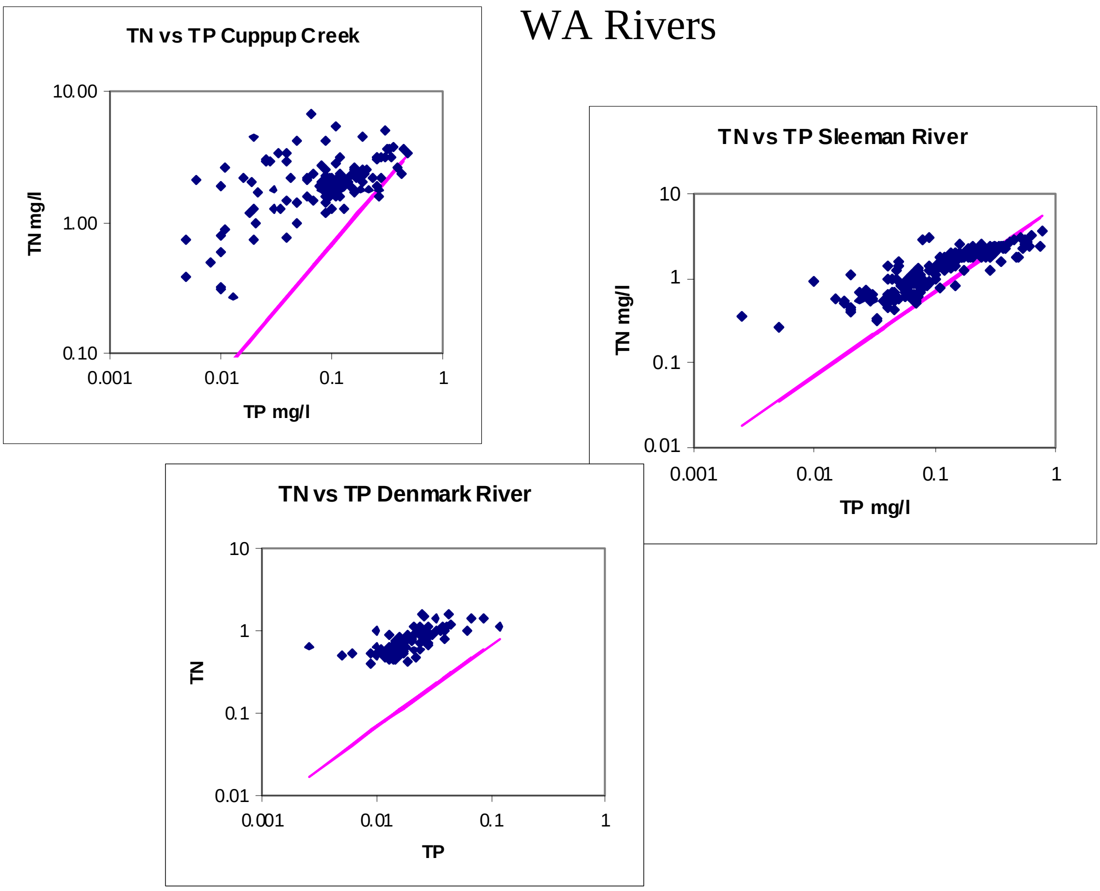


Figure 15: Water quality data from three rivers in the Albany Region. Data from WRC files courtesy of Malcolm Robb. Plots of TN:TP showing high N:P ratios in the more dilute waters. The thin diagonal line is the Redfield ratio line for reference.

DIN:DIP Plots WA rivers

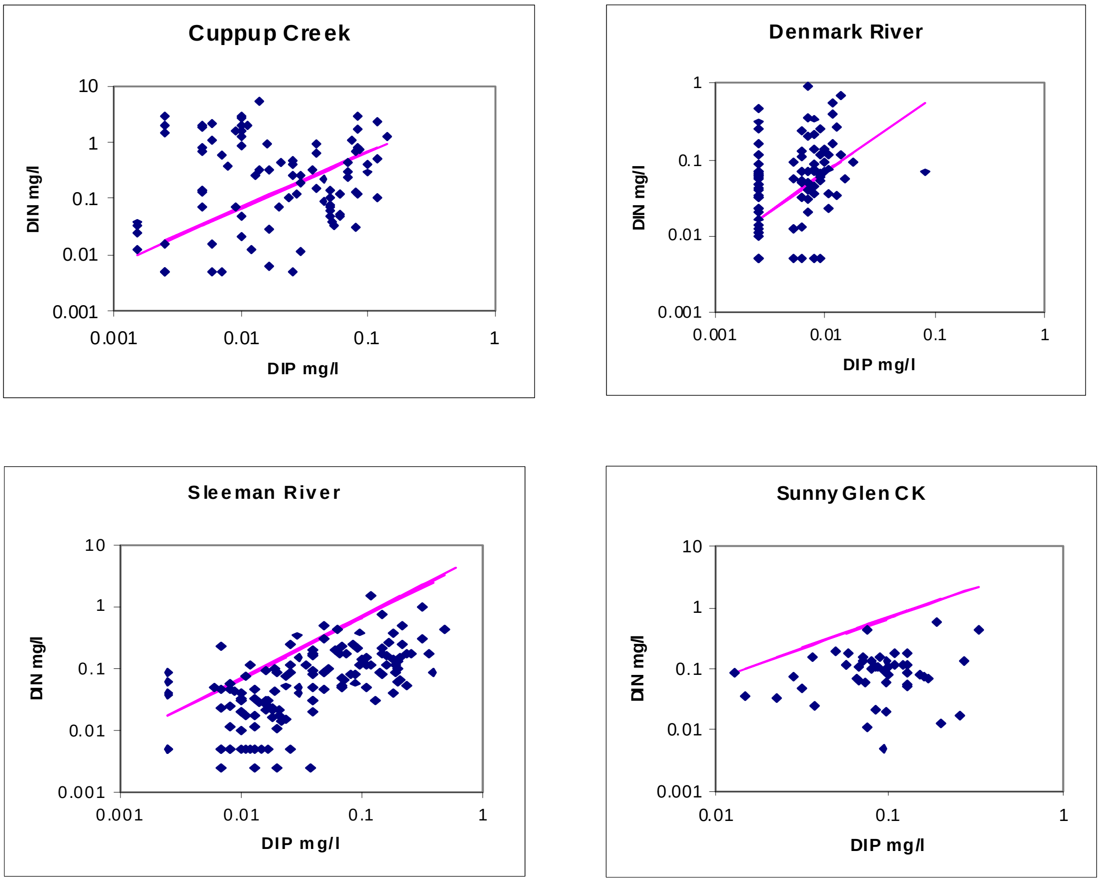
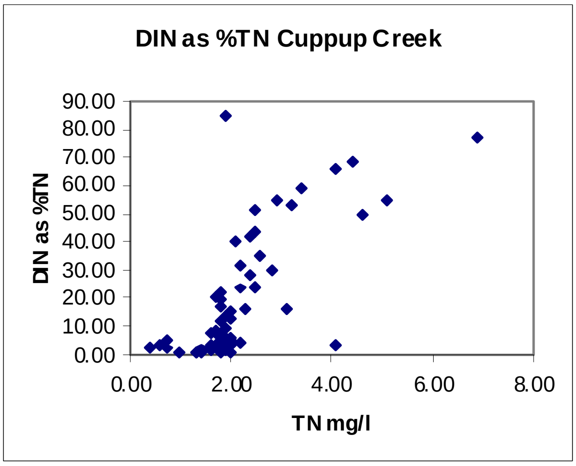


Figure 16: DIN:DIP plots for four rivers in the Albany region of WA. Data from WRC files courtesy of Malcolm Robb. The thin diagonal line is the Redfield ratio line for reference.

Two basic patterns of DIN and DIP as a proportion of TN and TP were revealed. Either the proportion of DIN and DIP increased as the TN and TP increased (eg DIN as %TN, Cuppup Creek, Fig 17 – indicating saturation of the chemical and biological control mechanisms, as described above) or they decreased as TN and TP increased (eg DIP as %TP, Denmark River, Fig 17). High DIP as %TP at low TP were either related to the high mobility of DIP in sandy soils (Gerritse and Adeney 1992) and to the iron status of the soils in the catchment (Weaver et al. 1994, 1996, Weaver and Prout 1996, Weaver and Reed 1998), or to the low uptake of DIP in rivers, which flow seasonally and do not have a large biomass of riparian vegetation. Disappearance of the DIN was due to biological uptake by ecosystem components – either by primary producers or by denitrification. These patterns of DIN and DIP variability with TN and TP provided an explanation for the variability in the cross-plots of DIN vs DIP as shown in Figs 12 and 14.



WA Rivers, Albany

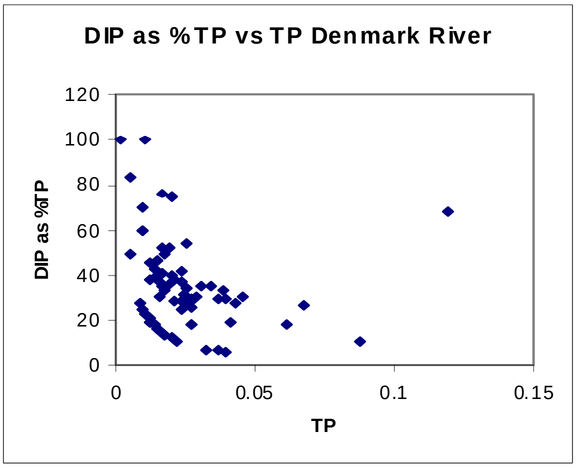


Figure 17: Plots of DIN as %TN and DIP as %TP for data from Cuppup Creek and the Denmark River showing contrasting patterns.

Combining the DIN and DIP data from the various catchments produced plots that showed distinct minima in both DIP as %TP and DIN as %TN when plotted against TP and TN (Figs 18, 19). These data were difficult to interpret until it was realised that the ecosystem model described in the introduction produced exactly the same result (Fig 20). As the loadings of N and P to the ecosystem model were increased, the proportions of DIN and DIP initially declined, only to rise later as the loadings saturated the biological responses. These ecosystem simulations were run with low biomass in all functional components and the components were allowed to grow and interact as the model ecosystem response developed. Clearly these results were obtained because the DIN and DIP minima corresponded to the point where either by biological uptake (and/or the binding of DIP by iron) the DIN and DIP proportions were reduced to a minimum. In short these minimum points corresponded to the point of strongest interaction of biology and chemistry (mP/2 plus iron chemistry) with the catchment loadings.

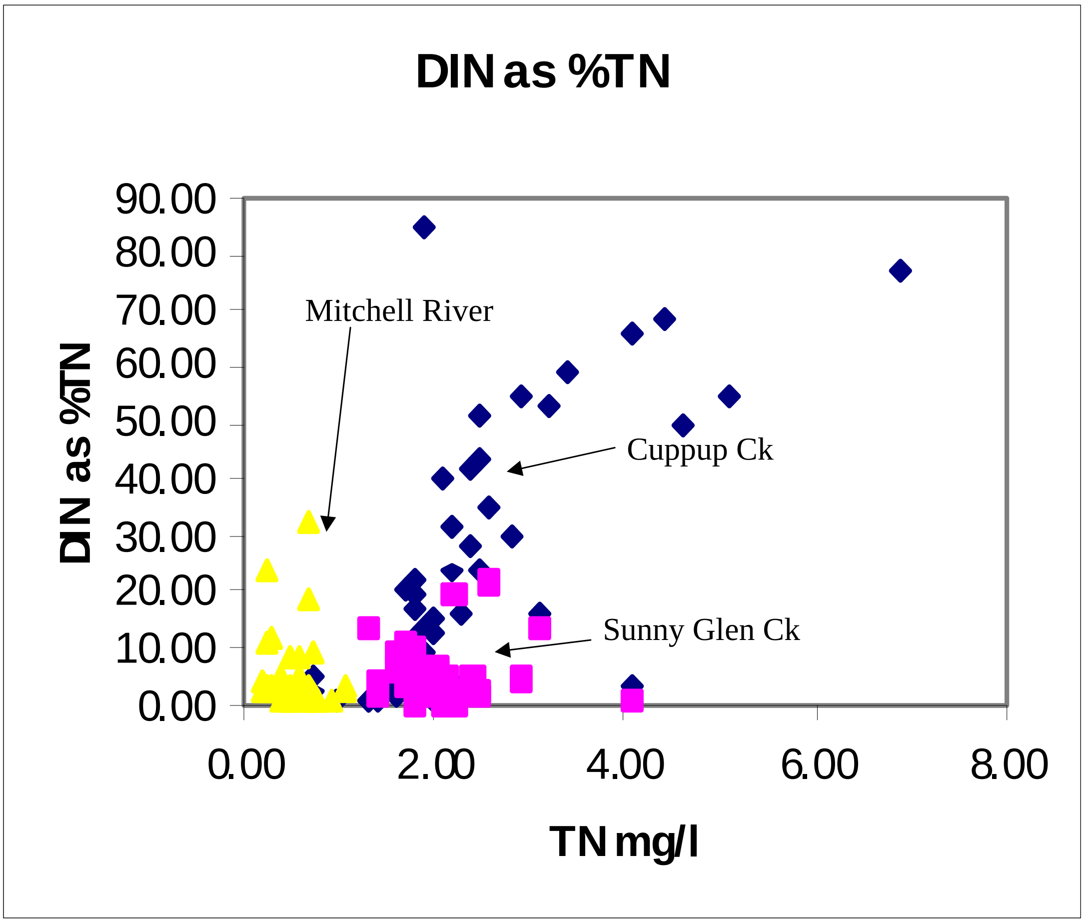


Figure 18: A plot of DIN as %TN for the three labelled rivers in the Albany region of WA. Showing regions of reducing DIN, a minimum and then a rise to saturation.

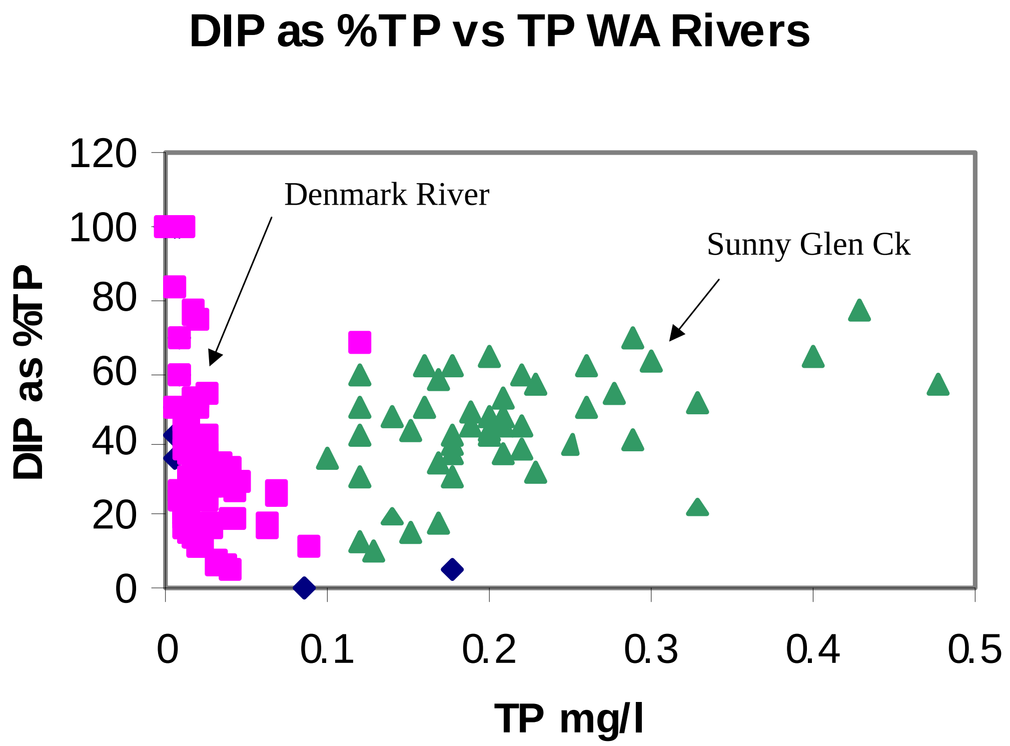


Figure 19: A plot of DIP as %TP for two labelled rivers in the Albany region of WA.

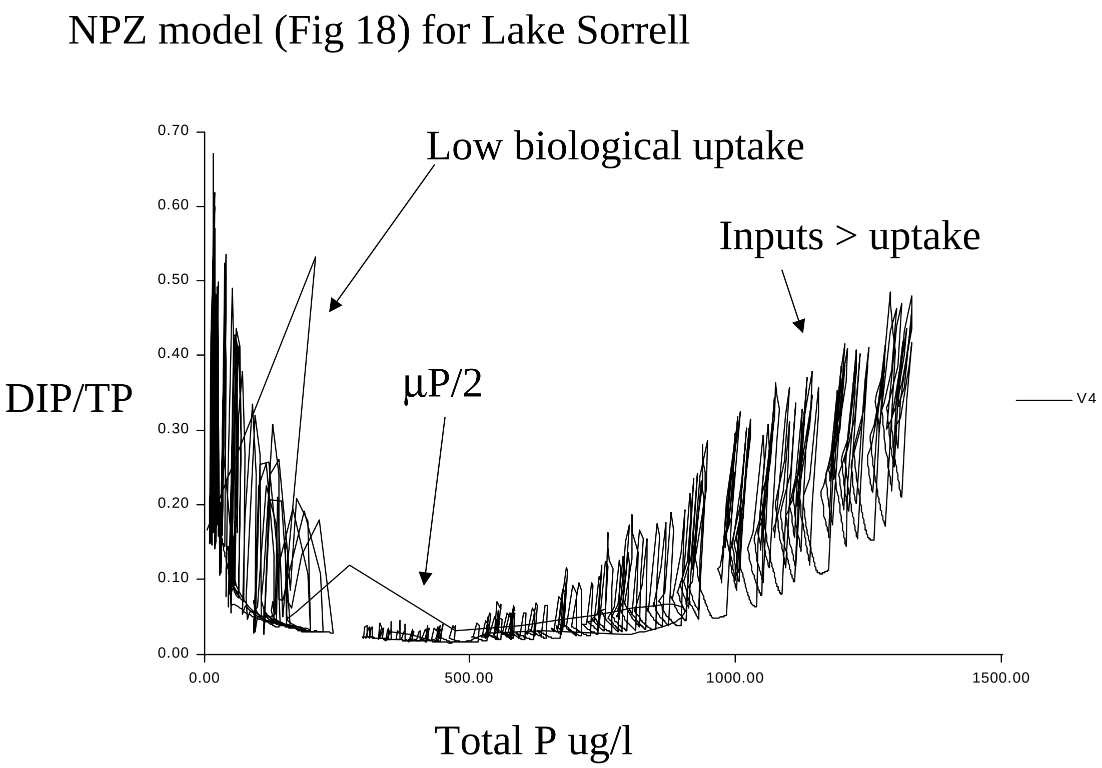


Figure 20: Output from the coupled pelagic and benthic model (Fig 8) showing the same patterns of DIP as %TP as the data from the WA rivers shown in Fig 19.

The interpretation of these data was clear. Allochthonous effects, from C:N and N:P ratios in catchment loads, determined the basic TN:TP and TKN:TP responses in the water column (Fig 21) with in-stream effects becoming more prevalent in richer waters and a decline in the ratios towards (or even below) the Redfield line. The DIN:DIP responses were dominated by the balance of loads which saturated the in-stream processes and the uptake and/or removal of DIN and DIP by denitrification and iron complexation on clay surfaces (Fig 22). This provided a framework for further interpretation of these data. More analyses of these data will be required when a more detailed knowledge of the land use and soils of each catchment are obtained.

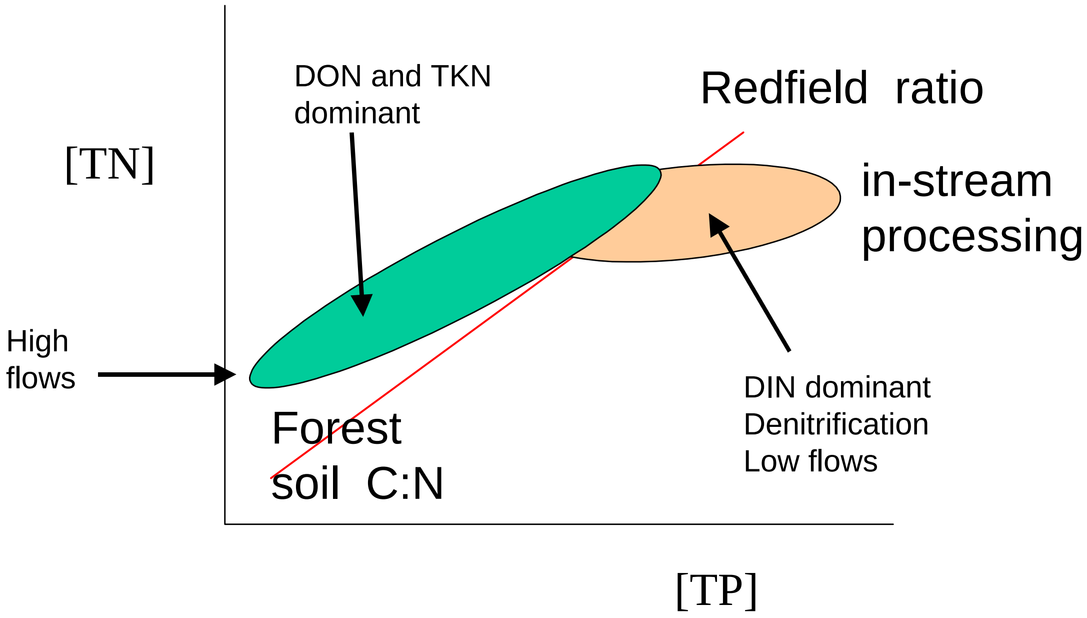


Figure 21: A schematic diagram explaining the various regions of the TN:TP plots for rivers.

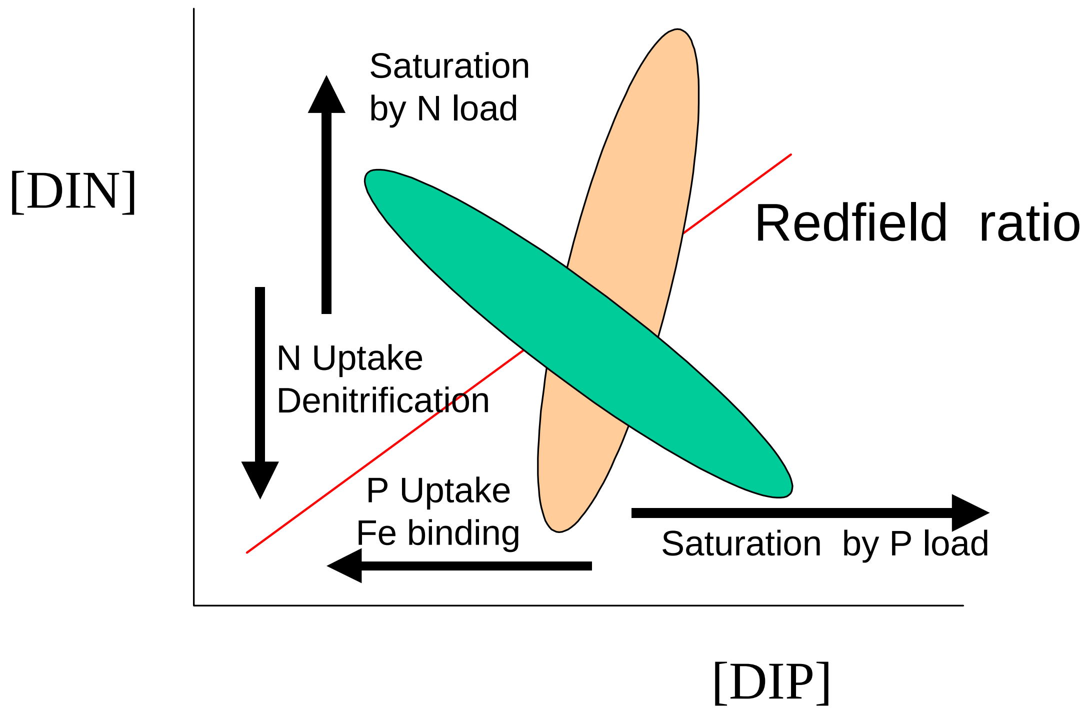


Figure 22: A schematic diagram explaining the processes underlying the DIN:DIP plots for river water quality.

3. The Hawkesbury-Nepean River, NSW

(Kerr 1994) published an excellent set of water quality data from the Hawkesbury-Nepean river system in NSW. These data were analysed by Harris (2000) and were replotted as Fig 23. In brief they showed saturation of the DIN as %TN plot due to high loads in this highly modified catchment (as expected from the Sydney catchment export data) and some buffering of the DIP and %TP plot by clays, iron and organic interactions in the river. Most of the DIP values were between 30-50% of TP with a few higher values. A plot of TN:TP or DIN:DIP for the Hawkesbury-Nepean river (Fig 24) showed broad correspondence with the Redfield line but very high TN:TP and DIN:DIP ratios in many cases. The TN values in this river were boosted both by high TKN and by high DIN from wastewater treatment plant (WWTP) outfalls along the river. For many years there has been a large program of P removal from these WWTPs resulting in high N:P loading ratios from the plants.

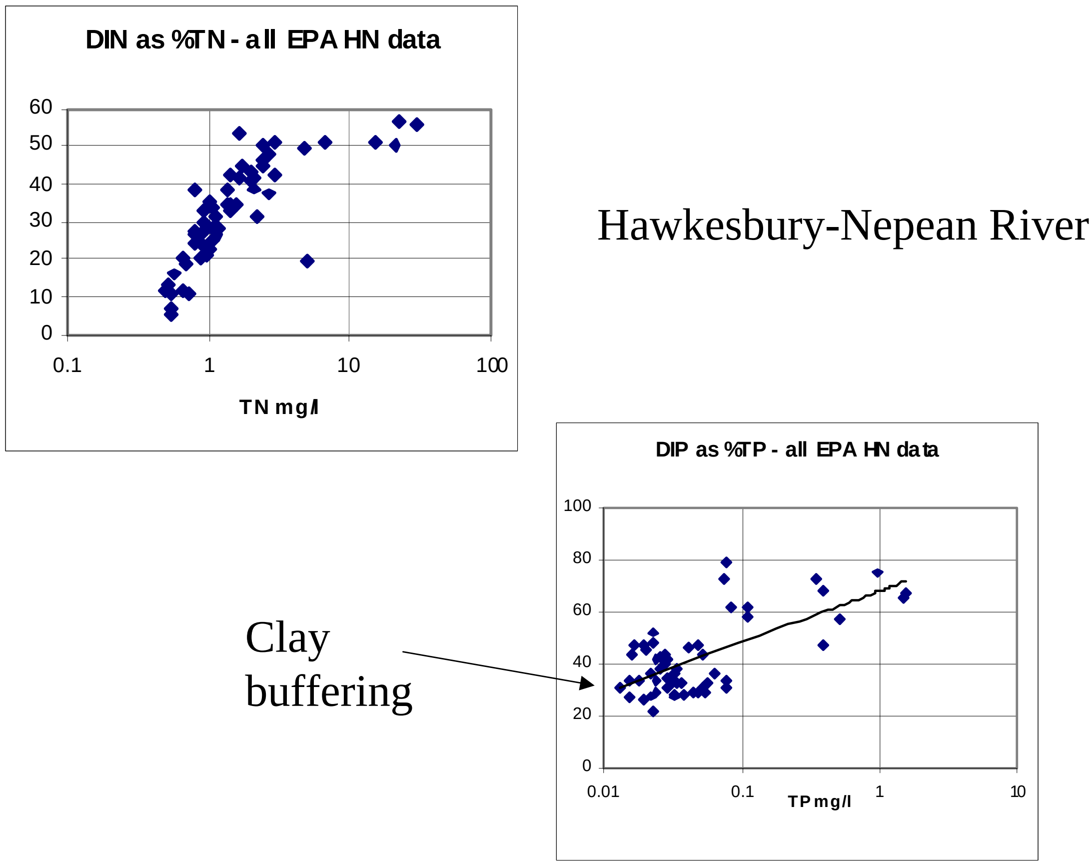


Figure 23: Plots of DIN as %TN and DIP as %TP for EPA data from the Hawkesbury-Nepean river. Data from Kerr (1994). The DIN as %TN behaves as predicted by the model in Fig 8, whereas the DIP as %TP data shows buffering of the DIP proportions by interactions with clays, iron and TOC in the water.

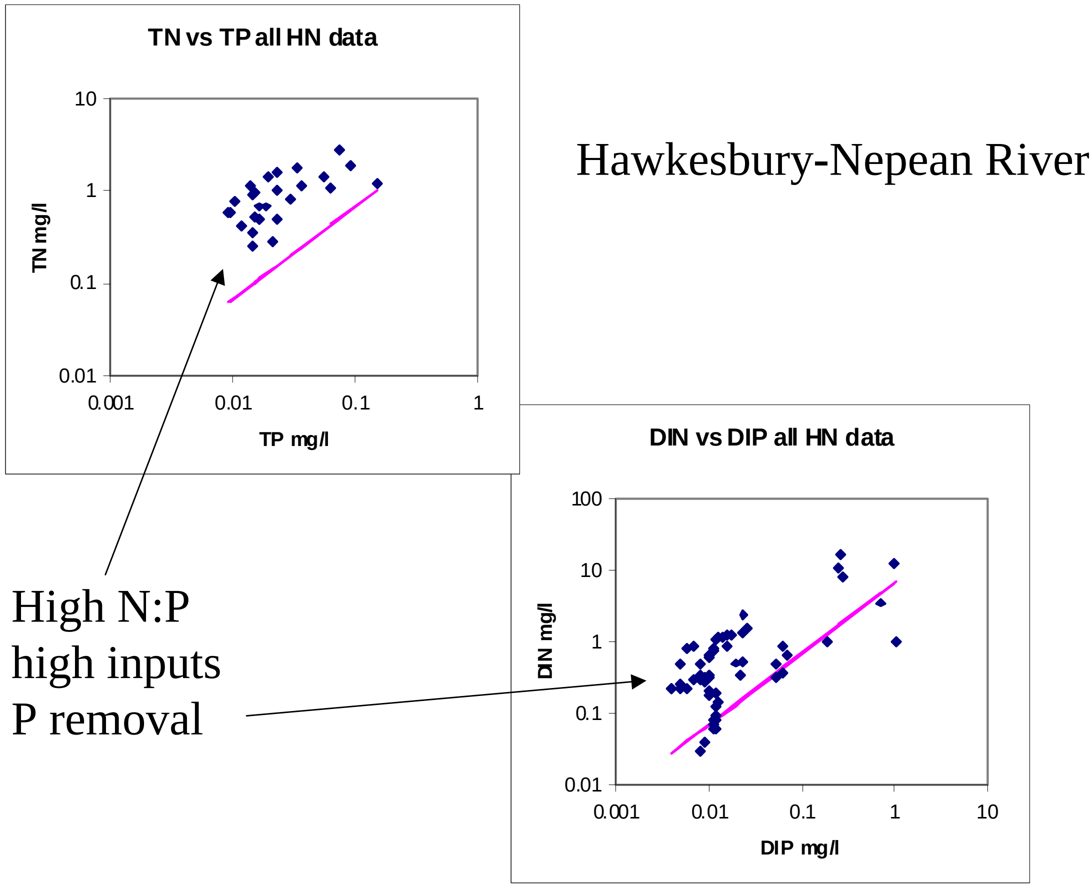


Figure 24: Plots of the TN:TP and DIN:DIP data for the Hawkesbury-Nepean from Kerr (1994).

Data sets from the MDB were analysed – in particular a long-term data set from the Murray River (Mackay et al. 1988). These data were also analysed by Harris (2000). Harris noted that the patterns of TN:TP ratios were as expected – ratios above Redfield in the more dilute waters, falling towards the Redfield ratio at higher concentrations. The one unusual feature of the data was the very low nitrate concentrations in these long residence time rivers – which could only be attributed to biological uptake and/or removal by denitrification. Indeed, as Harris (2000) pointed out plots of DIN as %TN were the reverse of the coastal and short residence time rivers (Fig 25) and showed very low nitrate concentrations at high TN. Harris (2000) also noted the correspondence between these data and the abundance of cyanobacterial blooms in warm, stratified, low nitrate waters with long residence times in weir pools and impoundments.

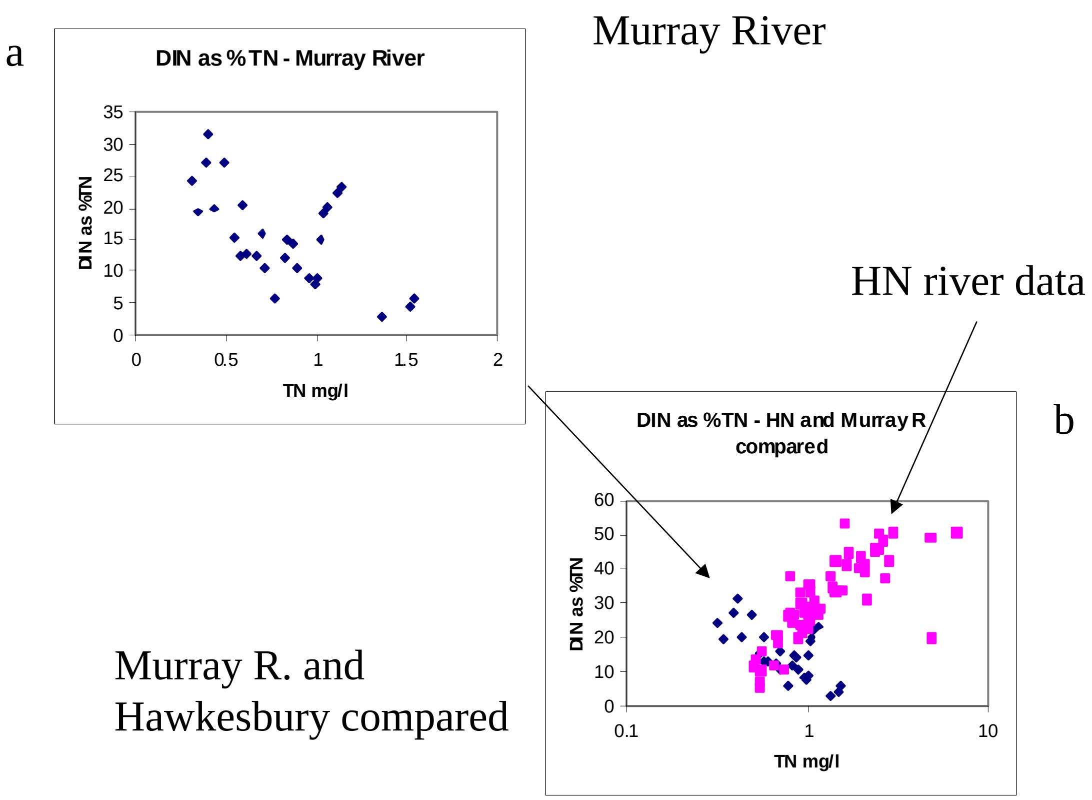


Figure 25: (a) A plot of DIN as %TN for the Murray river data showing a decline in DIN as TN increases. (Data from Mackay et al. 1988). (b) A comparison of the data from the Murray and the Hawkesbury-Nepean (see Fig 23 for comparison.)

A plot of DIN:DIP for the larger set of Victorian data showed many data points above the Redfield line – as expected from agricultural catchments (Fig 26) – with one or two points below the line from river systems in the inland. Comparisons of forested and agricultural catchments in Victoria showed, as for the NSW catchment exports, increases of all water quality parameters in agricultural catchments, but a most marked increase in nitrate (Fig 27, see also Harris 2000). A clear effect of land use and water residence times was therefore demonstrated in these data – clearing and development of agricultural land use increased all catchment exports (and nitrate in particular, eg Oyarzun et al. 1997), while ponding of the water and increasing water residence times in impoundments and weir pools removed the nitrate to very low concentrations.

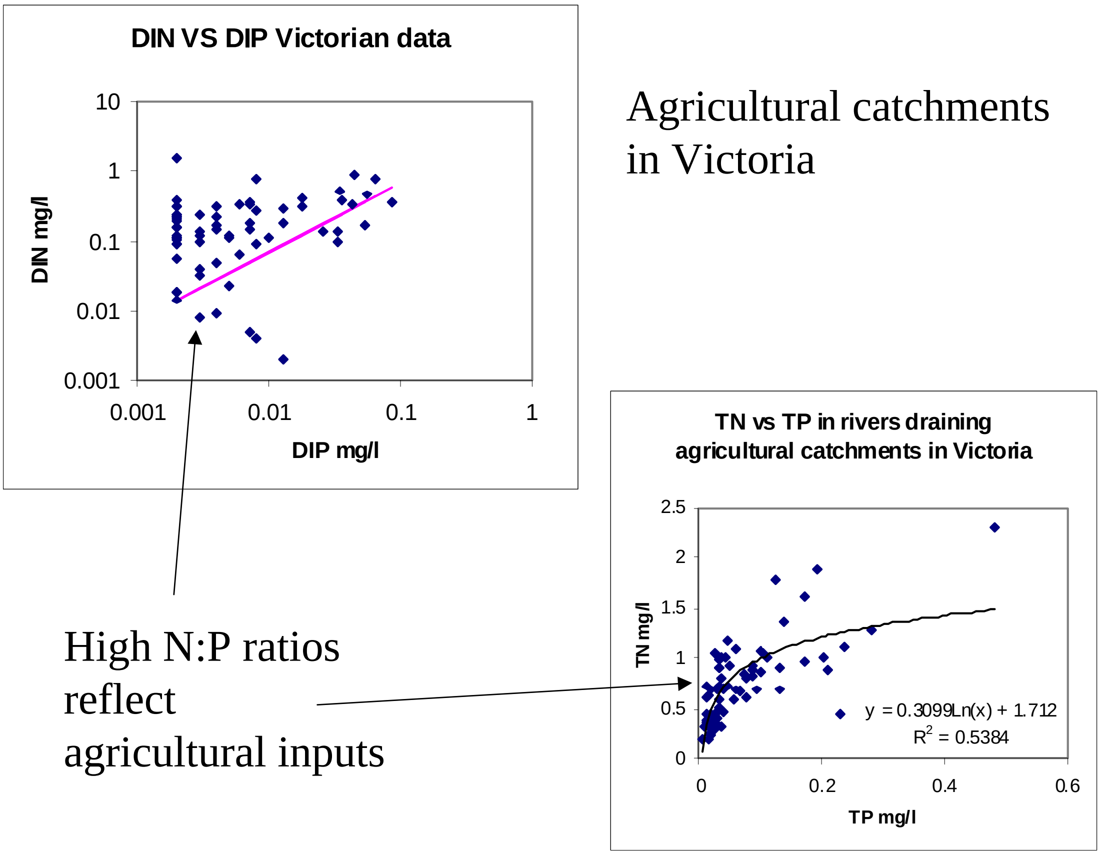


Figure 26: Water quality data from agricultural catchments in Victoria. Data from Cottingham et al. (1995). High DIN and TN concentrations reflect increased N loads from agricultural catchments.

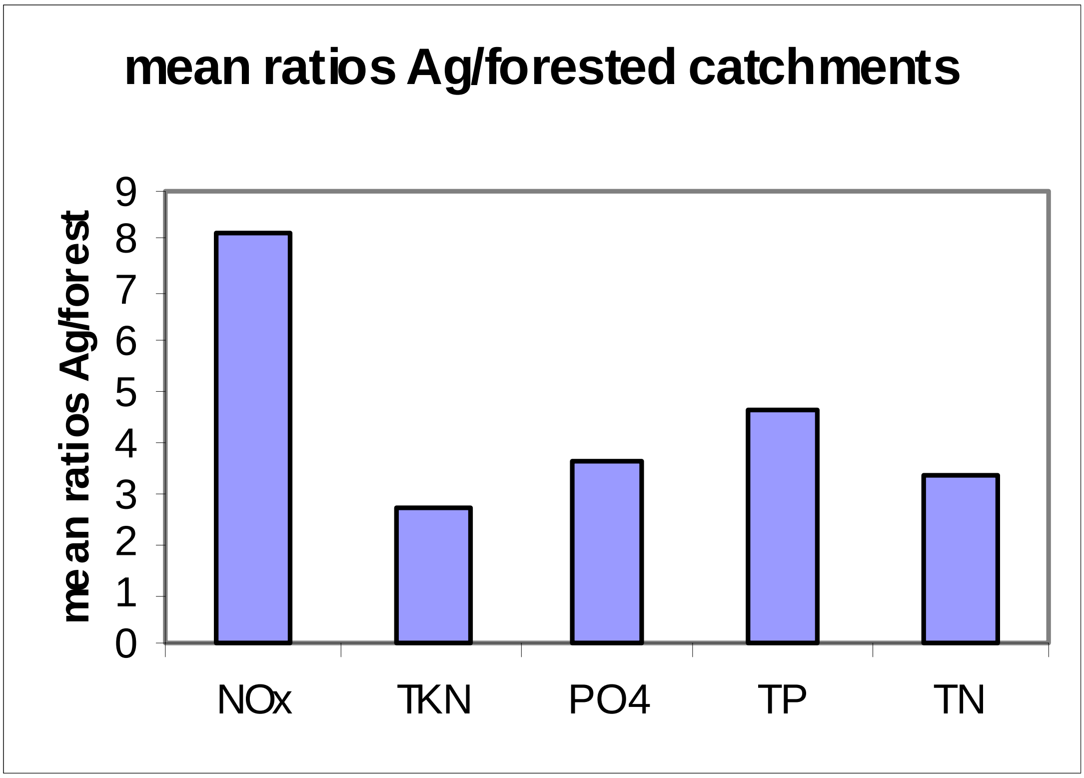


Figure 27: Mean ratios of water quality parameters measured in forested and agricultural catchments in Victoria. Data from Cottingham et al. (1995). While all parameters increase as land is cleared (by a factor of 2-4X), nitrate increases more rapidly than other parameters (by about 8X). (Compare to Fig 16.)

Analysis of data from the Liverpool Plains (DLWC 1996, 1997, 1998a,b) produced a similar result to that observed in the Murray River (Figs 28, 29) in that nitrate values were also very low (Fig 28). Plots of DIP as %TP and DIN as %TN showed the same kinds of responses as the WA data (Fig 29) and plots of TN:TP and TKN:TP (TKN by difference as there were no direct measurements) showed a number of points well below Redfield ratios (Fig 29).

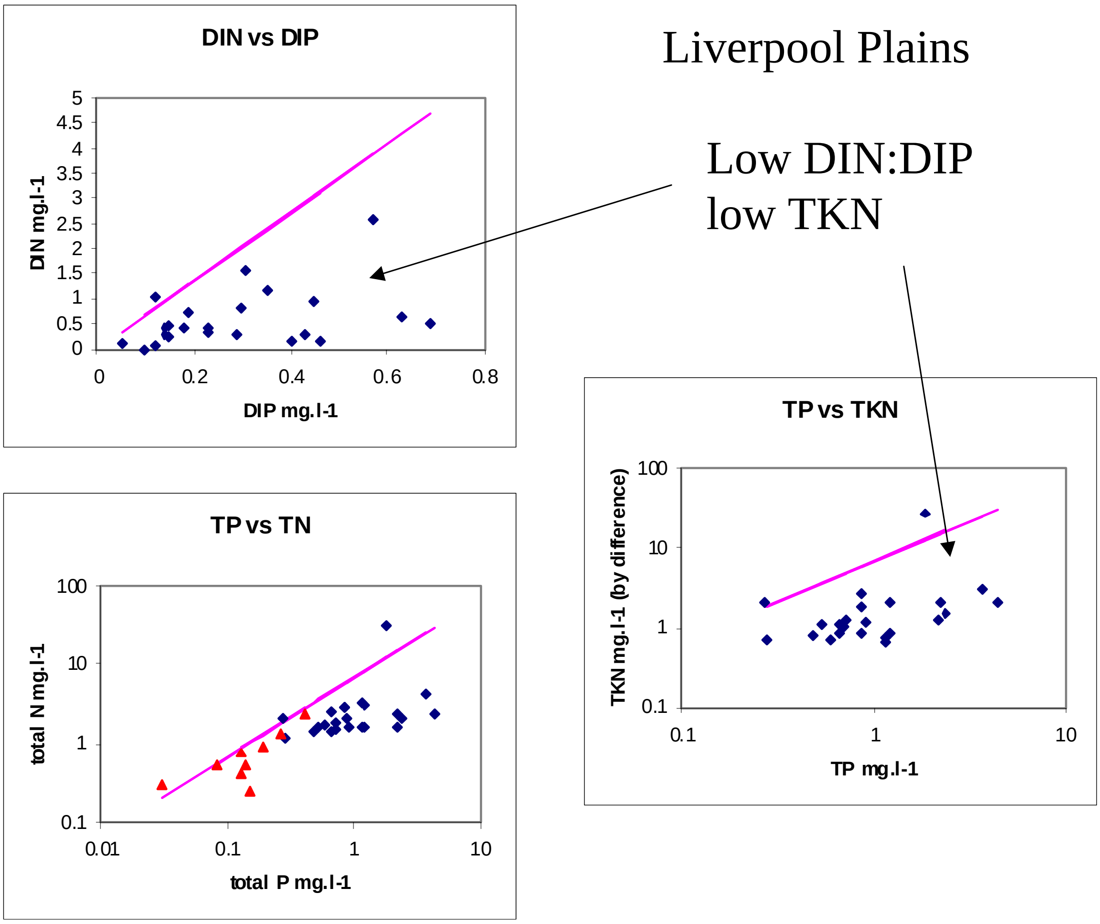
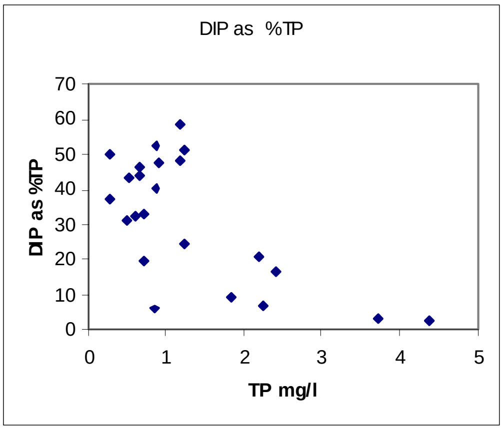


Figure 28: Plots of water quality data from river stations on the Liverpool Plains. Data from DLWC (1996, 1997, 1998a,b). The thin diagonal line is the Redfield ratio line for reference. Note the low TN:TP and TKN:TP ratios.



Liverpool Plains

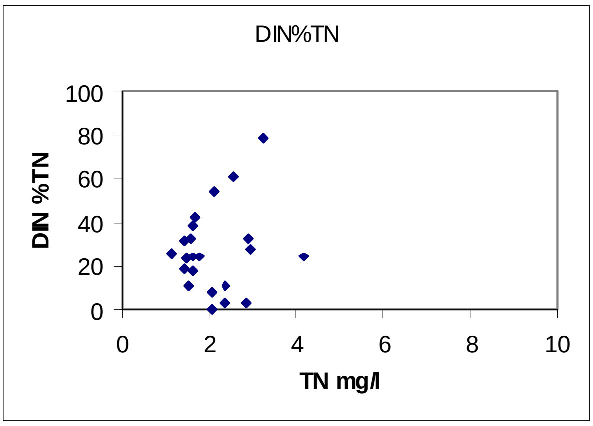


Figure 29: Plots of DIN as %TN and DIP as %TP for data from the Liverpool Plains. Data from DLWC (19996, 1997, 1998a,b).

Again nitrate was markedly reduced in these inland river samples but, surprisingly, TKN:TP ratios were below Redfield – clearly some process is removing DON from these waters, or else the loading ratios of N:P are less than might be expected. As far as could be seen from the data in DLWC reports (DLWC 1996) the loading ratios were close to Redfield ratios and although the TN:TP ratios were apparently less than those from the River Murray and other Victorian catchments there was no indication of major losses of TN in the catchment loads. I shall discuss one identified reason for the reduction in TKN in river waters below.

Effects of reservoirs, impoundments and wetlands on downstream water quality

1. Reservoirs and impoundments

A number of data sets were found that provided information about the water quality of impoundments (see Norris et al. 1991a,b and references in Harris 2000). Only one good data set however, gave sufficient resolution to give a good nutrient budget, that of Ebsary (1987a,b) for Mount Bold Reservoir in SA. The peculiarity of Australian reservoirs is that the residence time of the water ranges from a few days during floods to practically infinity during drought (Harris and Baxter 1986). Thus nutrient budgets for reservoirs must be obtained with a sufficient resolution to account for water inflows and outflows; and the nutrient inputs and outputs during periods of high and low water flows.

It was clear from a cursory analysis of some of the water quality data from reservoirs (Harris 2000) that these water bodies acted as sinks for TN and TP and frequently, sources for ammonia or nitrate. The widespread occurrence of hypolimnial anoxia meant that these water bodies were acting as large-scale anaerobic digesters, metabolising TKN (or DON) to ammonia and discharging it downstream where it was subsequently nitrified. Over the 12 year period of Ebsary's (1987b) studies, Mount Bold reservoir retained 56% of the TP input, 37% of SRP, 68% of PP, 42% of TKN, 26% of TN and –5% of NOx. The reservoir consumed TKN and was a net exporter of nitrate downstream; so Mount Bold had a negative net retention of nitrate. Others (Hern et al. 1981, Straskraba 1999) have noted this effect elsewhere and Walker and Hillman (1982) noted this same phenomenon in the Hume Dam. In some reservoirs nitrate exports were some 30X the inflow concentrations (Norris et al. 1991a,b, Harris 2000). Harris (2000) also showed that when flushed by storm events – and hence when residence times were also short – Australian reservoirs were net sources of TP (Fig 30). The retention of TN and TP in Mount Bold was compared with a random sample of a number of US lakes (Figs 31, 32), quoted in US EPA reports (Canfield and Bachmann 1981, Hern et al. 1981). On this basis the retention of N and P by Mount Bold Reservoir was little different from these northern hemisphere lakes.

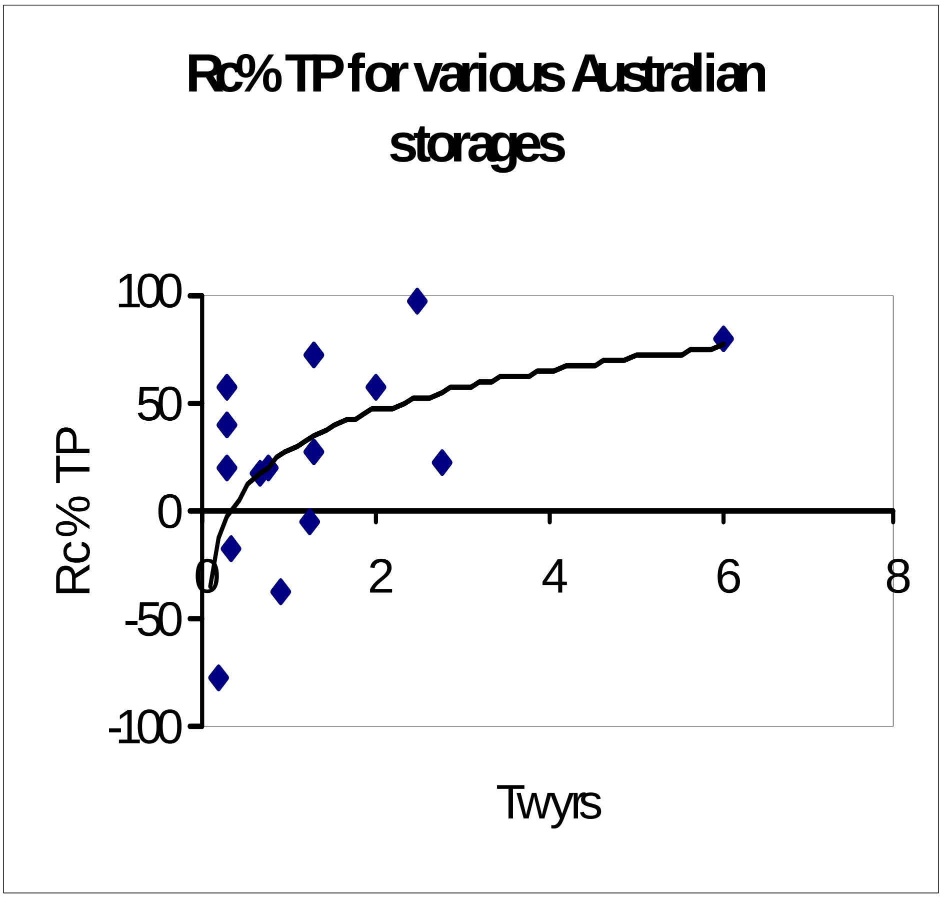


Figure 30: Data for the phosphorus retention coefficients of Australian impoundments as Rc% plotted against water residence times. Analysis of Harris (2000) from data in Norris et al. (1991a,b). At low water residence times (ie when flushed by high flows) these water bodies are sources of P (ie Rc% is negative.)

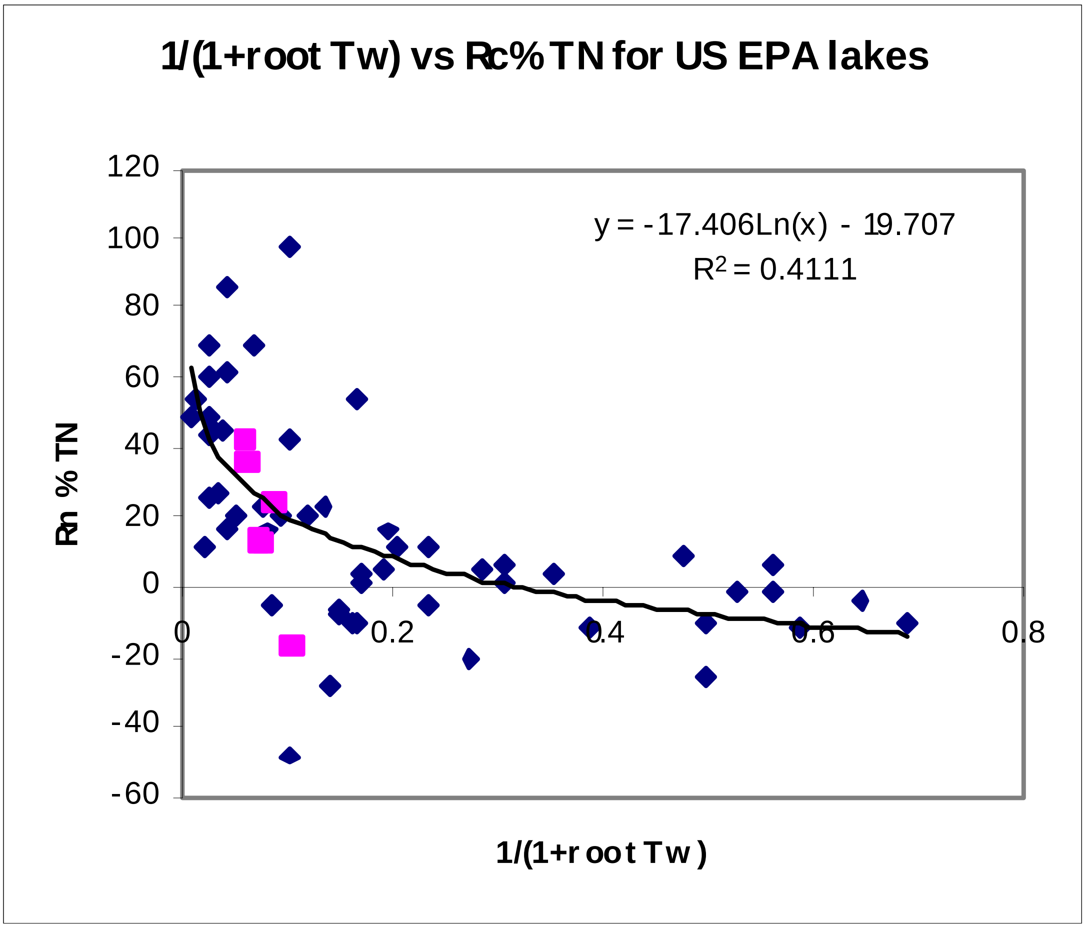


Figure 31: A comparison of the nitrogen retention characteristics of Mount Bold reservoir in Adelaide (pink squares, data from Ebsary 1987a,b) and a large sample of US EPA data for American lakes (Hern et al. 1981). Note the negative values for shorter retention times.

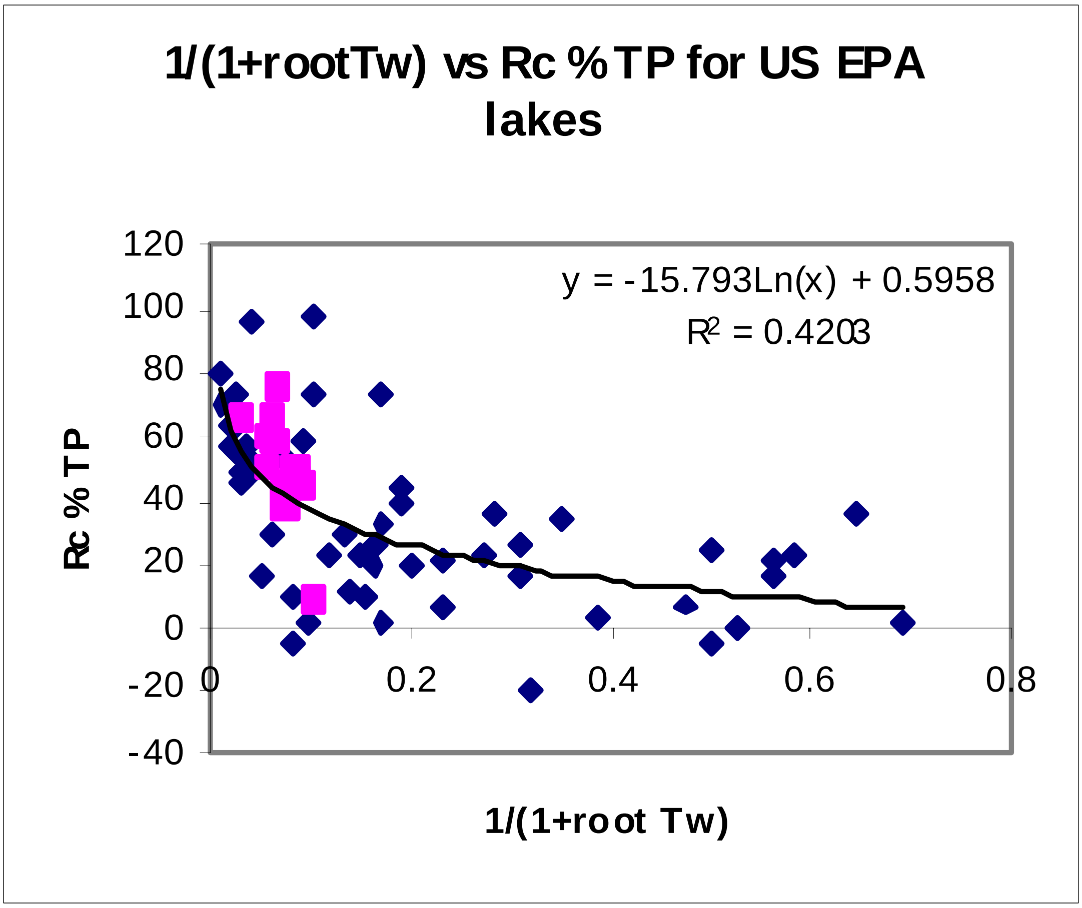


Figure 32: A comparison of the phosphorus retention characteristics of Mount Bold reservoir in Adelaide (pink squares, data from Ebsary 1987a,b) and a large sample of US EPA data for American lakes (Hern et al. 1981).

The surface water chemistry and the N:P stoichiometry of surface waters in Queensland impoundments showed strong N uptake and/or denitrification. This contrasted with the anoxic hypolimnetic waters rich in phosphate, ammonia, iron and manganese (Zaw and Chiswell 1999). N:P ratios in surface waters were found to be very low in a number of SE Queensland impoundments sampled by QDNR in the years 1994-4 (Fig 33). This might have been predicted based on their long residence times during low flow periods (Harris and Baxter 1996). The overall chemistry of P in these impoundments was surely a function of the chemistry of iron and manganese. Zaw and Chiswell (1999) found that these elements were abundant in the hypolimnia of Australian impoundments. Indeed manganese is frequently a problem in waters used for drinking and other urban uses. The overall chemistry of iron and phosphate is modulated by the availability of sulphur in these impoundments and Donnelly et al. (1997) has suggested that sulphur inputs are an important determinant of reservoir chemistry and phosphorus retention.

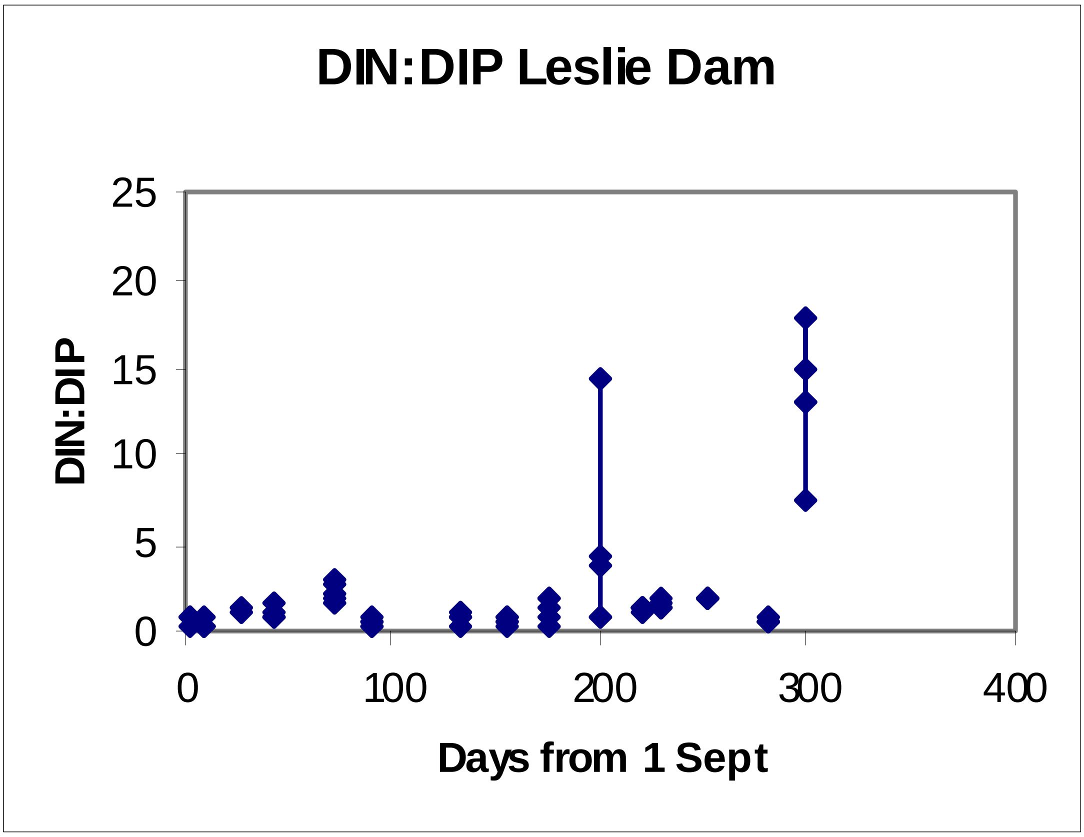


Figure 33: DIN:DIP ratios for surface water samples from Leslie Dam in 1993-4. Data from Queensland department of Natural Resources files. DIN:DIP ratios are very low indicating removal of N by denitrification or biological uptake.

Upstream reservoirs are therefore likely to have a significant downstream water quality impact as well as an effect on temperature regimes. Discharge of hypolimnial water downstream will release cold, anoxic water rich in ammonia (which is promptly nitrified as soon as river flow oxygenates the water) and also (depending on the sulphate concentration) rich in phosphate. TKN will be reduced as a result of decomposition processes in the reservoir.

These Mount Bold data are important. Straskraba (1998) showed that impoundments and reservoirs in the rest of the world were quite different in their phosphorus retention coefficients to lakes. In a large analysis of data from around the world he noted that topical and temperate impoundments were similar, but both were different from lakes. Nutrient retention is both a function of water residence time and of nutrient load (Ahlgren et al. 1988, Figs 9, 10). It was not clear from the data presented in Straskraba (1998, 1999) whether the higher phosphorus retention coefficients of impoundments were due to their generally higher nutrient loads (because impoundments generally have larger catchments, more altered land uses and higher nutrient loads than lakes) or to other intrinsic differences between lakes and reservoirs. It has already been demonstrated that P exports from Australian catchments are generally lower than those overseas (Caraco 1995). The good comparison between N and P retention in Mount Bold *reservoir* and a large sample of US *lakes* (Figs 31, 32) showed that the differences between impoundments and lakes must be related to the generally higher nutrient loads in other parts of the world, and not to some other intrinsic differences.

2. Wetlands

All the international experience showed that wetlands were strong sinks for carbon (as DOC or biological oxygen demand), nitrogen and phosphorus (reviewed in Johnston 1991, Mitsch et al. 1995). As might be expected wetlands showed higher retention of C, N and P at low flows and, indeed, most of the international literature showed some simple relationships between retention and the hydraulic load (as the amount of water applied per unit area of wetland, Fig 34). While the retention of P appears to be a function of the chemistry of particles, iron complexes and clay surfaces (Oliver et al. 1993), the retention of C and N occurs in biofilms on the stems and roots of aquatic plants (Axler and Reuter 1996, Risgaardpetersen and Jensen 1997).

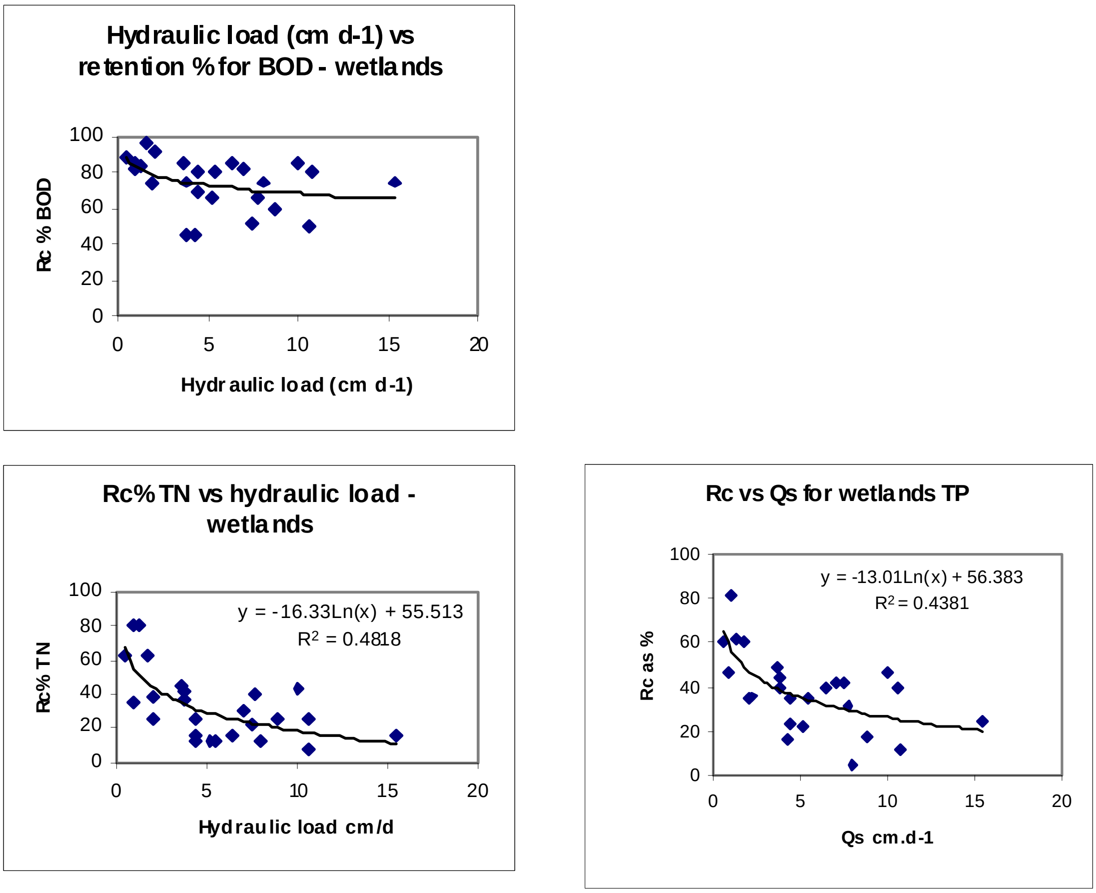


Figure 34: Retention coefficients for TN, TP and C (as biological oxygen demand) for wetlands sampled by Brix and Schierup (1989) plotted against the hydraulic load (in cm/day).

C in wetlands is partly stored in anaerobic sediments and, with much of the C stored being remains of higher plant and denitrification removing N the C:N ratio of wetland sediments is high. As Aitkenhead and McDowell (2000) have recently shown, the DOC exports from catchments are largely a function of the C:N ratios of parent soils and organic materials. Wetlands and peatlands in catchments are therefore usually disproportionately important in contributing to the DOC exports from catchments (Dillon and Molot 1997, Hinton et al. 1998). Drainage of wetlands will therefore tend to decrease DOC exports from catchments. There is also a strong linkage between iron export and metabolism and DOC exports from catchments (Dillon and Molot 1997).

From the small amount of Australian data (largely collected by Mitchell and others) there is no reason to believe that Australian wetlands perform any differently to the international norms (Mitchell et al. 1995, Raisin and Mitchell 1995, 1996, Raisin et al. 1997). Note that, like impoundments, wetlands can export ammonia during high flows (Fig 35).

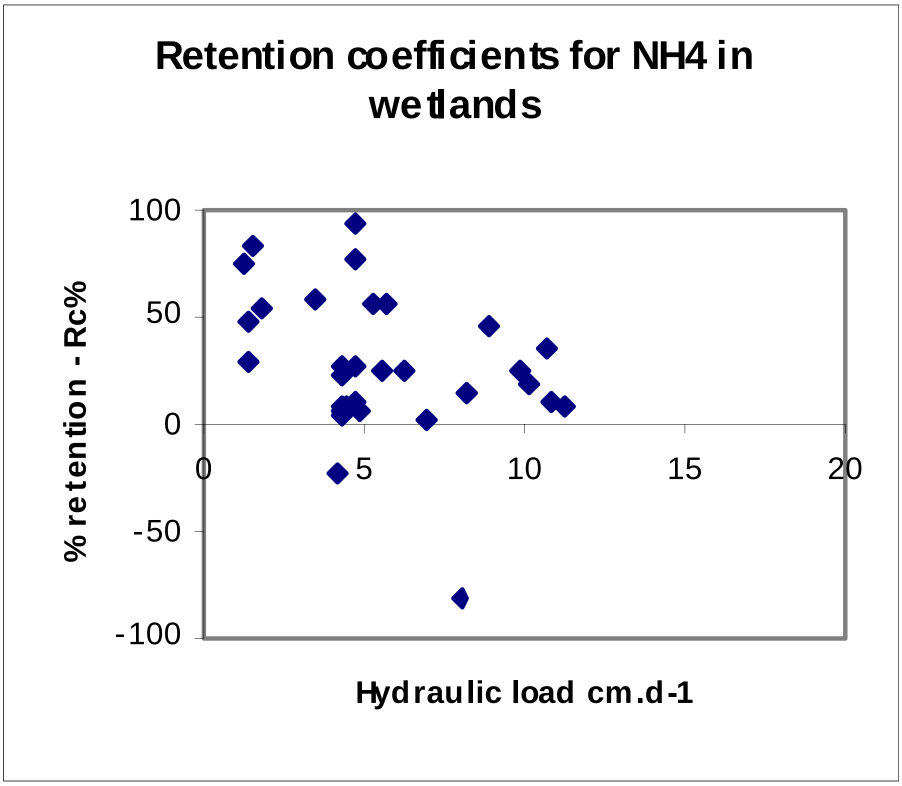


Figure 35: Retention coefficients for ammonia in wetlands sampled by Watson et al. (1989). Note that these wetlands may be sources of N at high flows.

Nutrient loads to estuaries and the ecological response

Water quality in estuaries is, like lakes, impoundments and other freshwater bodies, a function of the nutrient loads and processes occurring in the estuary itself. In the case of Australian estuaries N inputs tend to be low because the freshwater run off from the land is relatively low, water residence times in the estuaries may be long and water quality, frequently, a strong function of tidal flushing. Heggie and Skyring (1999) have provided a useful survey of the relationships of flushing to estuarine biogeochemistry. In other parts of the world catchment exports are high because of higher population densities and higher runoff (Howarth et al. 1996, Howarth et al. 1998), more intense agricultural development (Jordan et al. 1997) and because of high atmospheric deposition of nitrogen (Hessen et al. 1997)

Estuarine nutrient loads can easily be calculated from riverine water quality and hydrology and can be related to impacts on the ecology of these systems. Harris (2000) used data from a variety of sources (quoted therein) to determine the loads to a number of east coast NSW and Victorian lagoons and estuaries. Much of the data came from Scanes et al. (1998). These data are shown in Fig 36 and, as expected, the N and P loads were close to Redfield proportions – although the changing form of N was a factor as noted above. The changing forms of N were clear from the work of Eyre et al. (1999), wherein it was clear that the DON load from forested catchments to coastal waters raised the N:P ratio to higher than the Redfield proportions (Figs 37, 38) . Replotting the data from Weaver's work (op. cit.) showed a similar result from WA catchments (Fig 39). As discussed above, the occurrence of N:P loads at higher than Redfield proportions was a function of the C:N ratios in the forested source catchments. Replotting the data in Scanes et al. (1998) and Harris (2000) on the basis of catchment area gave a result (Fig 40), consistent with previous arguments about the interactions of runoff with N export.

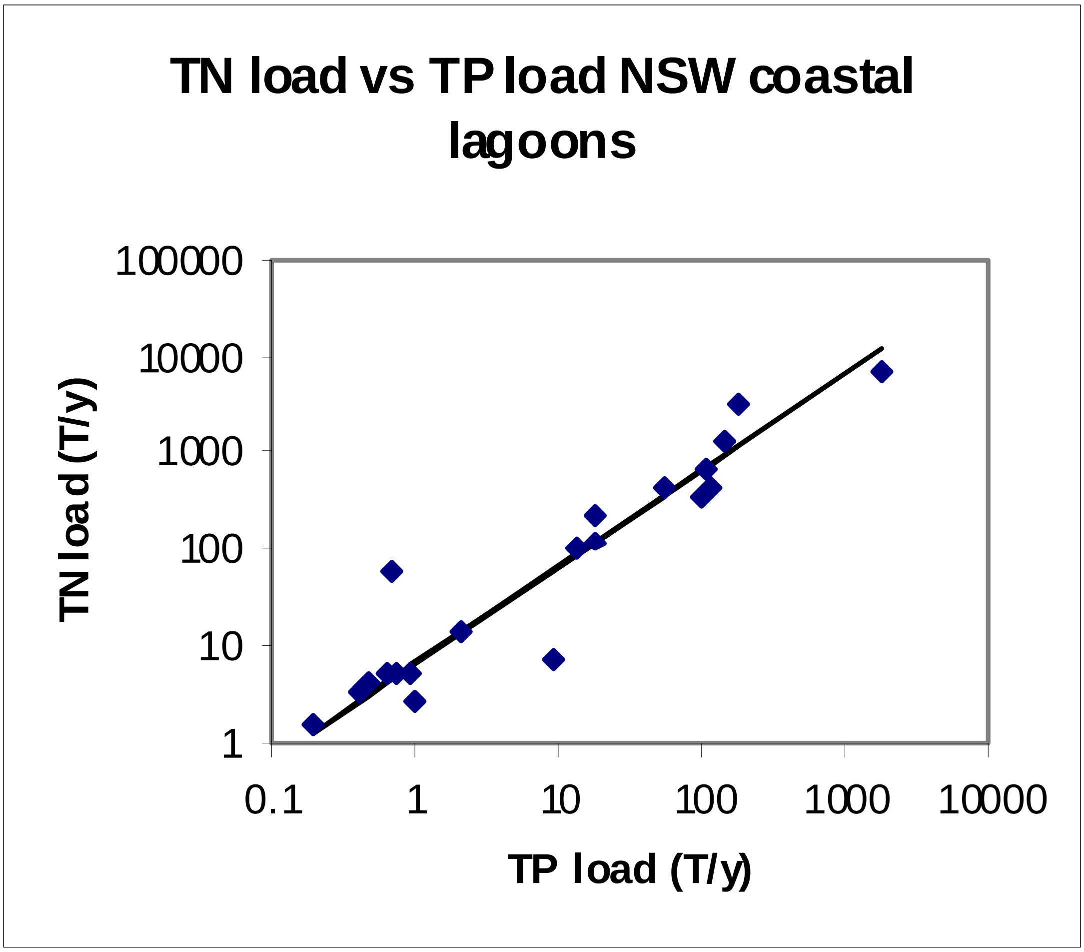


Figure 36: Loads of TN and TP to coastal lagoons in NSW. Data from Scanes et al. (1998) and Harris (2000). The thin diagonal line is the Redfield ratio for reference.

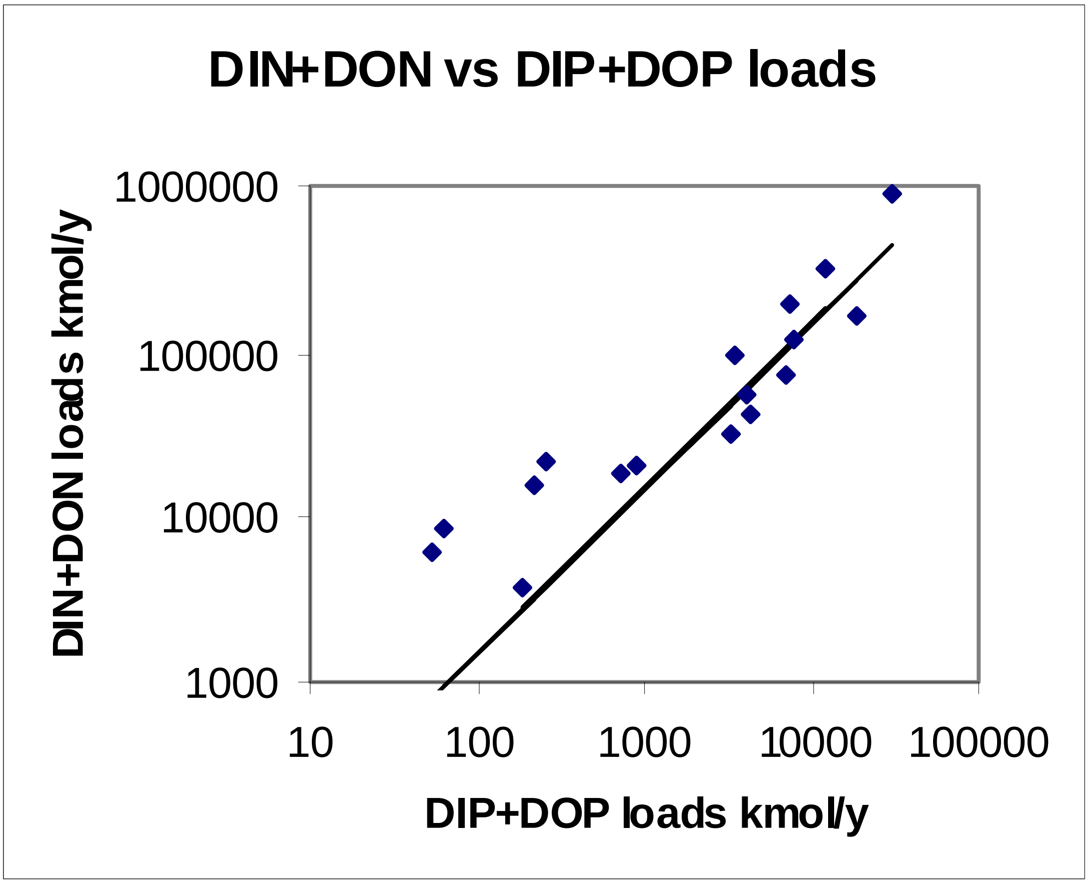


Figure 37: Loads of DIN and DON compared to loads of DOP and DIP for rivers in North Queensland. Data from Eyre et al. (1999). Note the increased N:P ratios arising from DOP exports from forested (low export catchments).

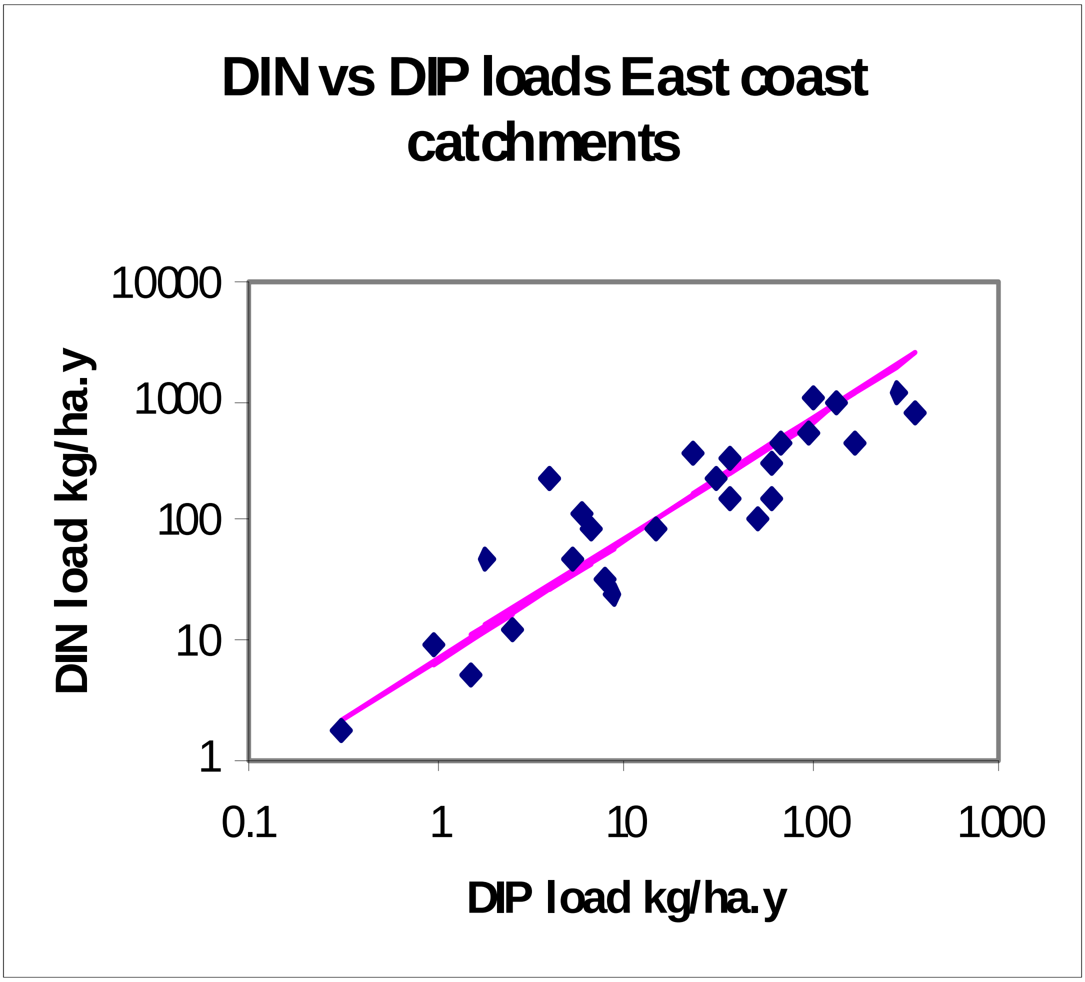


Figure 38: Loads of DIN and DIP to coastal lagoons. Data from Harris (2000). Loading ratios follow the Redfield reference line in these costal river systems.

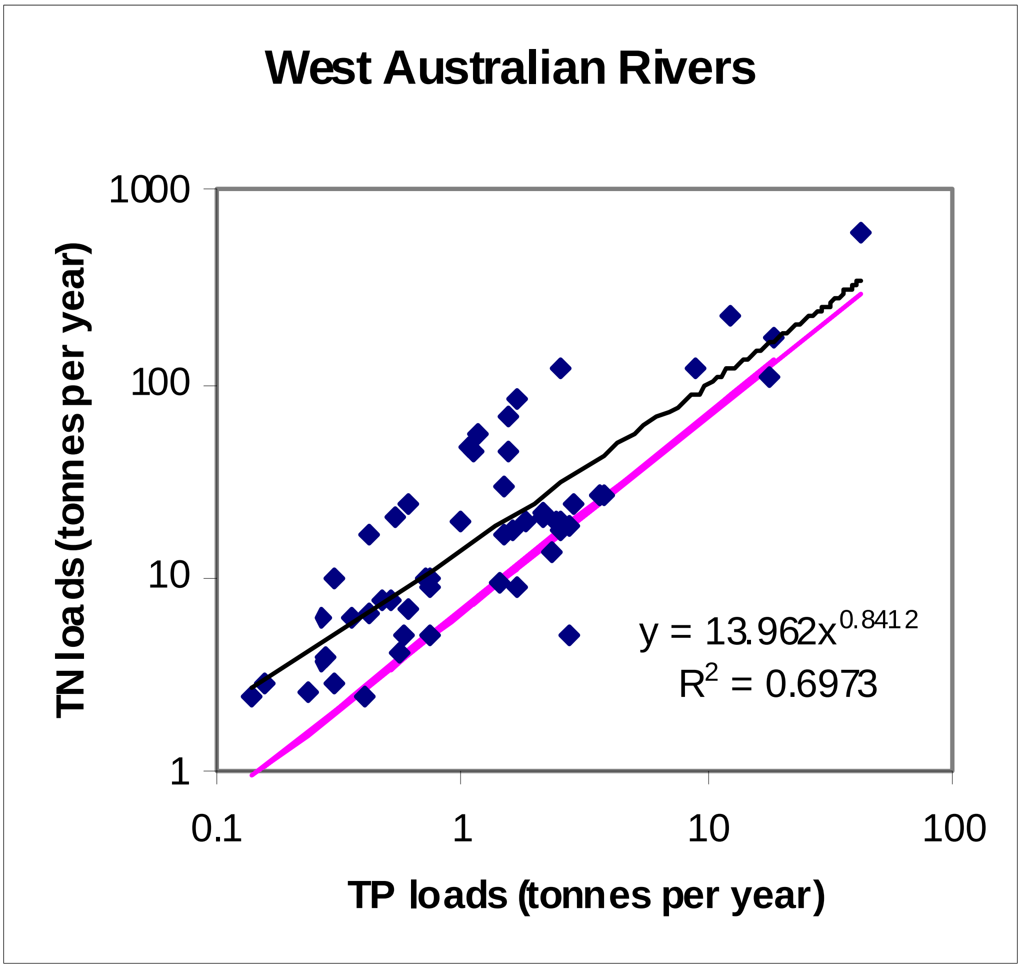


Figure 39: Loads of TN and TP to WA estuaries. Data from Weaver et al. (in South Coast Estuaries Project 1991a,b) As in the Swan and other WA rivers the N:P ratios are high from largely pristine catchments due to the high N:P and C:N ratios generated by these catchments.

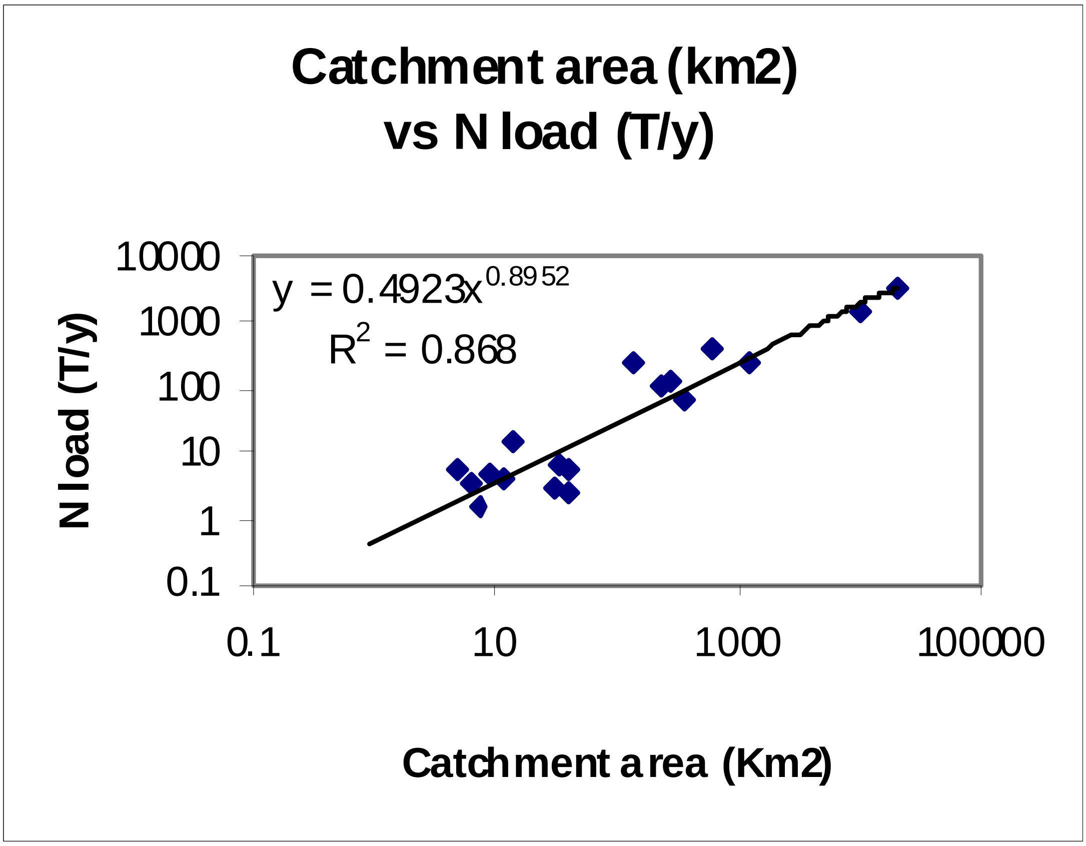


Figure 40: N loads to coastal lagoons in NSW and Victoria plotted as a function of catchment area. Data from Harris (2000).

Australian estuaries are predominantly N limited because of efficient denitrification of the N loads – and this seems to be true internationally (Hinga et al. 1995, Seitzinger 1987, 1988). Studies of the biogeochemistry of Australian estuaries and embayments (see eg Harris et al. 1996) have all demonstrated the importance of sediment denitrification in these systems. Heggie et al. (1999a,b) have provided good recent reviews and data. Harris (1999a) explained the basic differences between lakes and estuaries in terms of nutrient limitation and ecology. The differences are due to the different functional groups of organisms in freshwater and seawater. The importance of denitrification in Port Phillip Bay can be seen from the long term water quality data sets (Figs 41, 42, see also Harris et al. 1996). Harris (1999a,c) has explained the interactions of water column and sediments in estuaries and the resulting strong hysteresis effects with increasing and decreasing loads. These mechanisms are identical to the “two states” of lakes discussed above and the water quality of these estuaries and lagoons is strongly dependent on the presence of abundant macrophytic plants (in this case seagrasses). As long as abundant seagrasses are present, Australian estuaries have good water quality and nitrate is usually almost unmeasurable (Harris 1999a). Like impoundments N:P ratios in surface waters are very low.

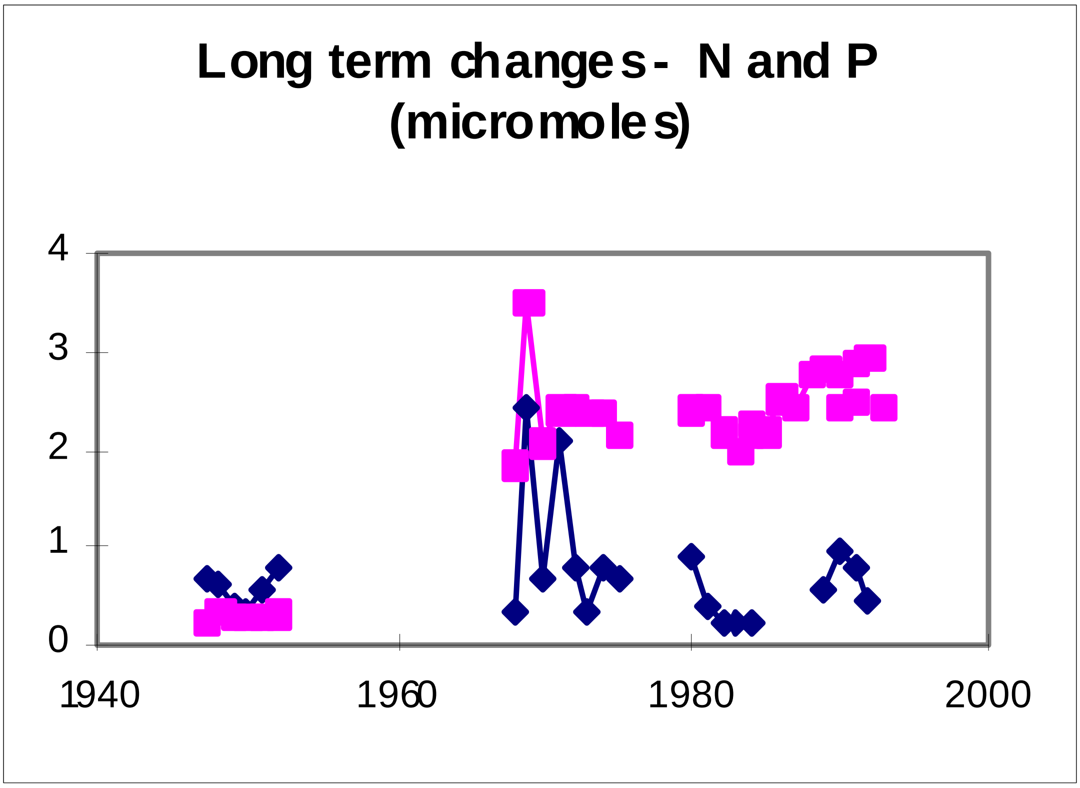


Figure 41: Long term water quality data from Port Phillip Bay (mean Bay wide concentrations for offshore stations) showing the steady rise in P concentrations over the years but the low concentrations of N, maintained by high denitrification efficiencies. Data from Harris et al. (1996)

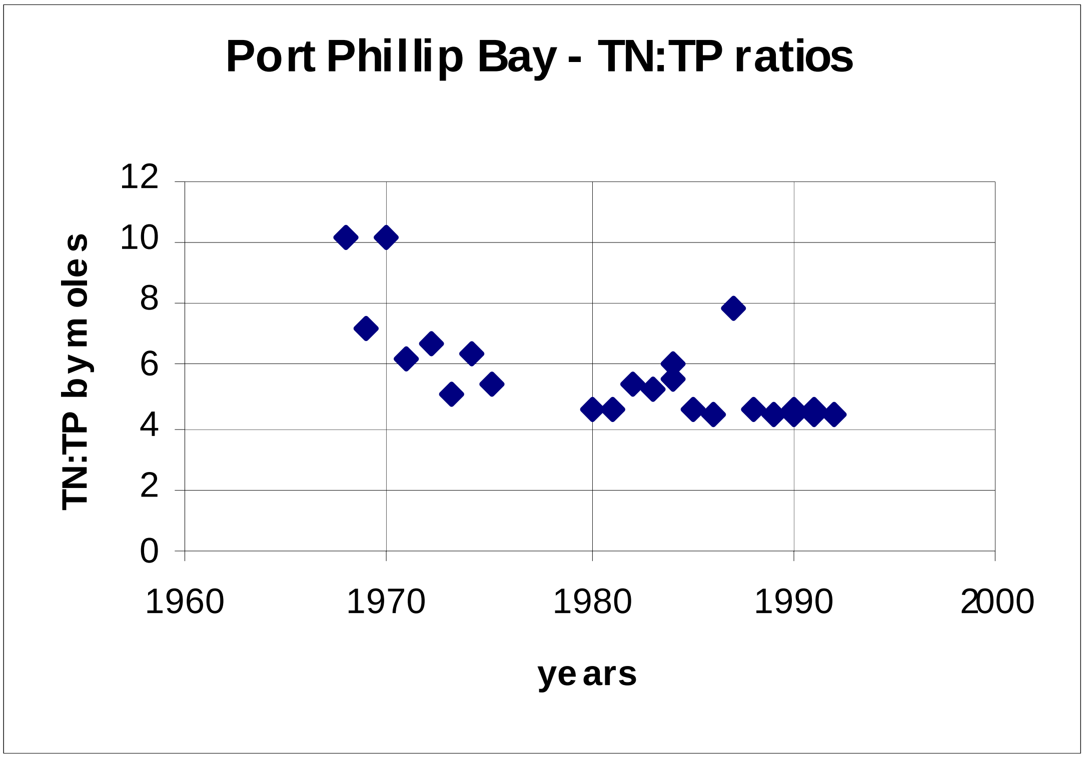
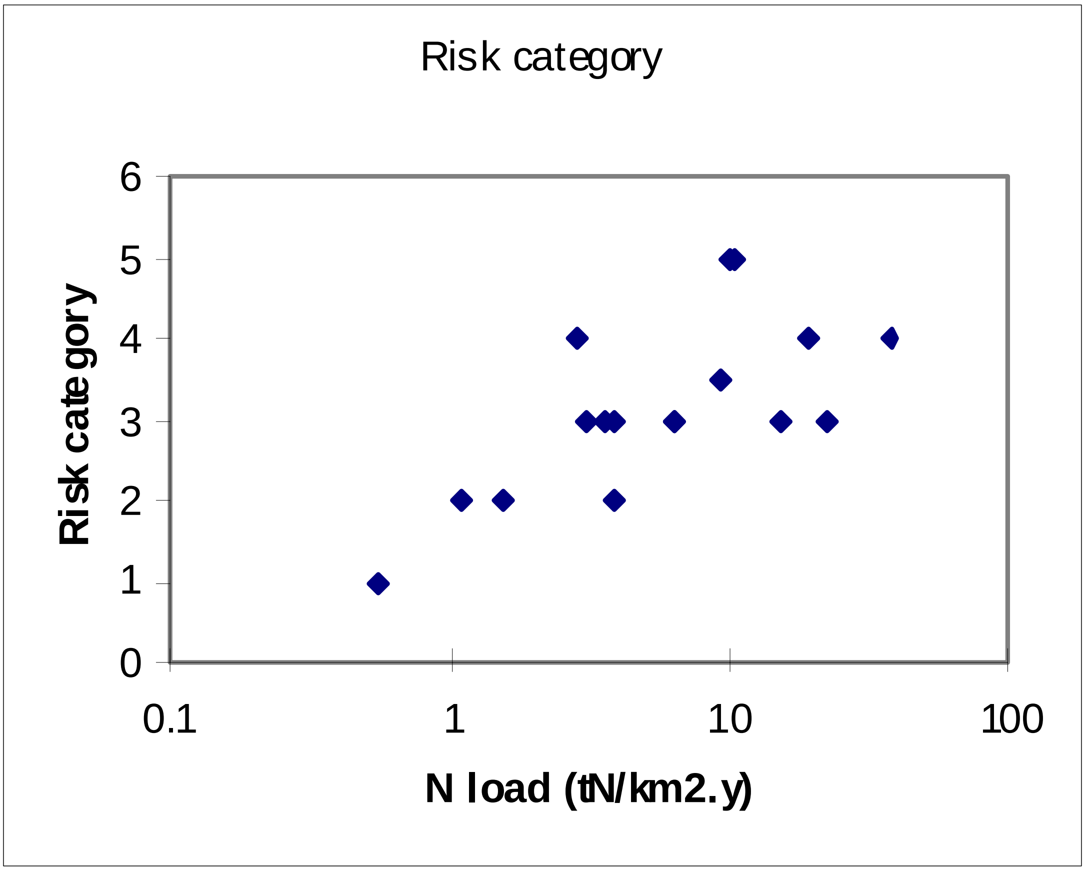


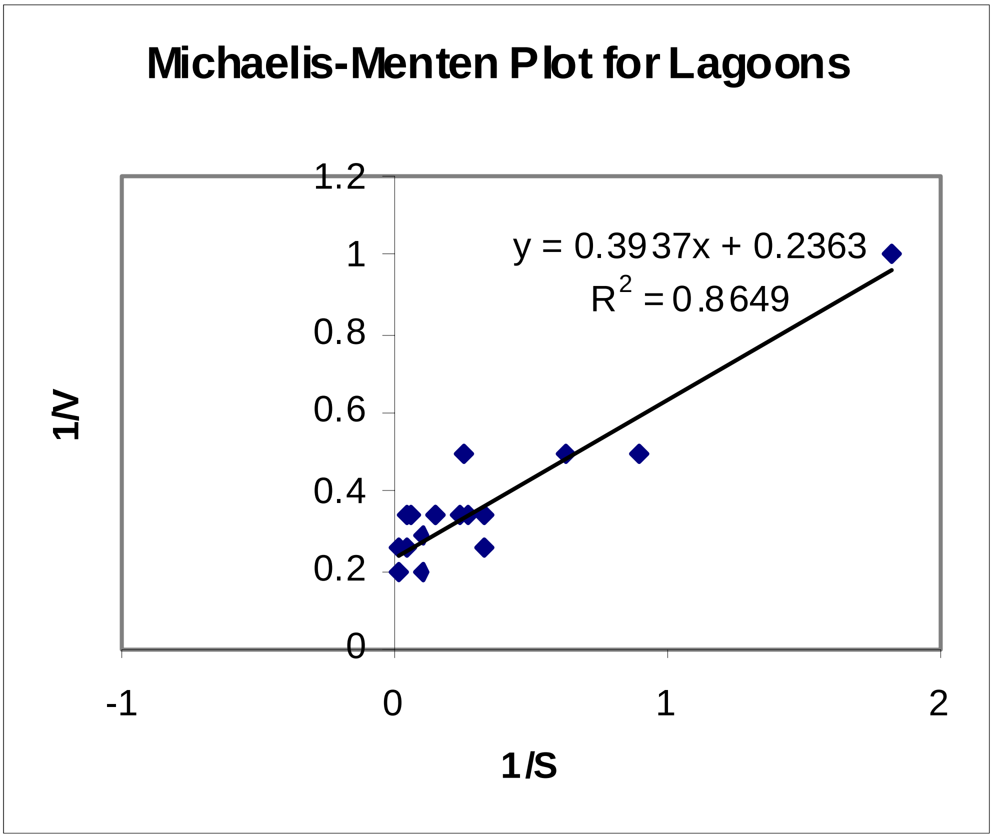
Figure 42: Mean bay wide TN:TP ratios for Port Phillip Bay have declined over the years as denitrification efficiencies have risen due to increased carbon loads (Harris et al. 1996). Like many coastal systems around the SE coast of Australia, Port Phillip Bay is strongly N limited.

Replotting the data of Scanes et al. (1998) and adding further data (Harris 2000) shows the degrading effects of increased N loads on Victorian and east coast NSW lagoons. The response of the lagoons was measured by a degradation scale of 1-5 (explained in Scanes et al. 1998), where 1 was pristine and 5 was heavily degraded as evidenced by abundant algal blooms and loss of seagrasses. Fig 43 shows the results of this assessment plotted against N loads (as tonnes of TN per square kilometre of water surface per year). Replotting a transformed data set (Fig 44) shows that, in effect, what was going on was the “titration” of entire ecosystems with nitrogen, a feat reviewed in a broader context by Kelly and Levin (1986). The half saturation point for these coastal lagoons was found to be a nitrogen loading rate of about 1.66 tonnes N per square kilometre of water surface per year. This is the approximate load of N at which Kelly and Levin (1986) found general release of N limitation in ecosystems and saturation of primary production.



NSW Coastal Lagoons

Figure 43: A risk assessment of a number of NSW coastal lagoons plotted against their N loads. Data from Scanes et al. (1998) and Harris (2000). 1. Pristine, 5. Severely impacted by eutrophication.



K_s for titrating whole lagoons = 1.66 tN/km^2.y

Figure 44: The data shown in Fig 43 replotted as a Michaelis-Menten plot. This allows an estimation of the half saturation load (the N load giving half the maximum impact). This half saturation point is estimated to be about 1.66 tonnes N per square kilometre of water surface per year.

Just like the effects of increased loads of nutrients and turbidity on Australian rivers and shallow lakes, hysteresis effects in coastal lagoons and estuaries are well documented and spring from similar causes (Harris 1997, 1998, 1999a,c, Scheffer 1998). Once sediment anoxia sets in the denitrification efficiency of the sediments is reduced to zero and the sediments become an internal source of recycled nutrients. Murray and Parslow (1999a,b) modelled this effect using data from the Port Phillip Bay Study (Harris et al. 1996). Water quality in these coastal lagoons is a function of sedimentary processes – and it is the ecosystem components in the benthos that control the overall system response (see Fig 8).

Synthesis and conclusions

What this paper has documented very clearly is that the water quality observed in rivers, reservoirs, wetlands and estuaries is a very direct function of catchment geology, land use and flow velocities. We should, therefore, take a landscape approach to understanding and managing water quality from hill-slope to estuary (Engstrom et al. 2000). Clearly land use change results in both changes to the hydrological balance of catchments (see eg Williams and Melack 1997) as well as changes to the biogeochemistry. Removal of more than 50% of the native plant cover results in increases in both the horizontal and vertical flows, so that runoff increases after rain and ground water becomes a more important influence on stream chemistry during low flow periods. This could be seen in the data that revealed strong effects of landscape clearance on stream salinity. Across wide areas of this continent stream salinity is a good integrator of the effects of landscape change in the catchment.

The major ion chemistry of Australian waters is clearly influenced both by the great age and deep weathering of the landscape, the underlying geology (Talsma and Hallam 1982, Banens 1987) and land clearing and its effect on soil chemistry and salinity (Wood, 1924, Sharma et al. 1980, Walker et al. 1998). Forestry and agricultural practices influence water quality (Gerritse and Adeney 1992, Talsma and Hallam 1982), as does urban development (Simeoni et al. 1994, Ferguson et al. 1995). We now realise that there is a much closer and more rapid connection between soil development, terrestrial vegetation patterns, land use and water quality than has hitherto been realised (Engstrom et al. 2000). It is not just dryland salinity that results from land clearing. Changing land use over quite short time scales alters many aspects of water chemistry. Agricultural practices lead to soil acidity and sodicity, both of which are visible in the stream chemistry. Aquatic chemists, biologists and ecologists have tended to see the water as rather separate from the land, this view will now have to change. To restore water quality and river ecology it will clearly be necessary to restore the land and its ecological function.

It is clear from these analyses that there are many more changes to water chemistry than merely those detected by exceedences of the ANZECC water quality guidelines. Catchment nutrient exports are a function of land use in ways that can be explained by some fundamental ecological theory related to habitat fragmentation and reduction in biodiversity. Clearly exceedence of the guideline values is most likely to occur once saturation of the biological uptake is achieved by high catchment inputs, either from fertilisers use, the application of animal wastes or through urbanisation (see eg Fenn et al. (1998) and Hessen et al. (1997) for a discussion in the context of atmospheric N inputs to northern hemisphere catchments). However these analyses show that there are many more processes at work and that interactions between the major ion and nutrient chemistries (TSS, TOC, Fe and TP) are critical to a fuller understanding of the underlying chemistry.

There is much more information in the water quality data bases managed by the States then has hitherto been extracted. A biogeochemical approach has revealed much useful information and the very close linkages between land use, soil characteristics and water quality. In particular, these analyses have revealed extensive interactions between land use, pedology and water quality at, what can only be, quite short time scales – measured in only a few years to decades. The precise links in space and time between alterations of land use pedological characteristics of the soils and water quality urgently require more investigation. The very recent and important paper by Engstrom et al. (2000) is a pointer to further work in this regard.

It is a great pity that more of the water quality data held in reports and data banks does not contain the full breakdown of C, N and P into all the organic and inorganic forms. Much of the data is merely TN and TP data with little or no carbon data. If we are ever to pick the full story apart is it clear that we will need to collect the full suite of C, N and P data – particulate and dissolved, organic and inorganic. We will need these data if we are to fully understand the complex but intimate linkages between land use and water quality in this country. Because of the peculiarity of the Australian landscape, hydrology and climate no one else can do this for us. We can refer to the international literature and it will provide us with background information and comparisons with overseas work (eg Russell et al. 1998) but only Australian data will enable us to understand our own landscapes and rivers.

As readers will by now have gathered, it is most important to look at the landscape ecology of nutrient retention, and the pattern and connectedness of land use, and the ecology of catchments, rivers, lakes, wetlands and impoundments. Each has their own nutrient source and retention characteristics (driven by the physiology of the major species). The resulting movement of nutrients and, finally, loads to coastal waters (both total loads and the form of that load eg DIN:TN ratios) depend on the water flow regimes and sequences of retention systems. Land use change led to marked differences in the form of N exported – largely DON and TKN from forested catchment. The proportion of DIP in P exports was frequently buffered by interactions with TOC and Fe in particles – so tended to be a more constant fraction of TP.

The most appropriate approach to use when studying N and P movement in aquatic systems is that of budgets and mass balances (House and Warwick 1998). This approach is widely used in the northern hemisphere where acid rain through nitrogen and sulphur deposition is a major problem. This problem has been discussed in a number of recent papers viz: Behrendt and Opitz (2000), Berge et al. (1997), Burns (1998), de Wit (2000), Hessen et al. (1997), Kozerski et al. (1999), Windolf et al. (1996).

When coupled with land use change and the landscape ecology of riverine corridors undergoing anthropogenic change, there are a series of cumulative non-linear interactions at landscape scales. This has been widely discussed in Europe and North America, especially in the context of nitrogen deposition in the northern hemisphere, by Arheimer and Wittgren (1994), Haycock et al. (1993), Henricksen and Hessen (1997), Hillbricht-Ilkowska (1999), Kaste et al. (1997), Jansson et al. (1994a,b), Jenssen et al. (1994), Johnston et al. (1990), van der Molen and Portielje (1999) and Welker and Walz (1999). The Australian biogeography, biodiversity and climate is unique, so only studies of Australian systems placed in the context of a thorough knowledge of the international literature will allow us to move forward and provide mangers with adequate advice.

Landscape analysis of this kind has revealed that Australia is different and that the results obtained were quite different from those seen elsewhere, particularly the northern hemisphere. Previous work on catchment exports in Australia noted that there are differences between Australia and the other continents (Young et al. 1996). The work largely concentrated on empirical estimates of export coefficients for different types of land use; and these have largely been only developed for TN and TP (Young et al. 1996, 1997). This approach has tended to miss the subtleties of the approach that uses and analyses the full suite of inorganic and organic, dissolved and particulate forms.

Using Vollenweider's (1968, 1969,1975, 1976) approach to mass balances for lakes (and it must be remembered that these were largely developed for deep, glacial, oligotrophic northern hemisphere lakes) it has been possible, over the years, to develop some general understanding of the behaviour of rivers, lakes and wetlands in terms of nutrient retention coefficients. These retention coefficients can be defined as the proportion of the nutrient load retained in any particular river reach, wetland or impoundment, defined as:

$$Rc = v / qs + v$$

Where Rc is the retention coefficient v is an apparent settling velocity for the nutrient (cm/day) and qs is the hydraulic load or water inflow rate (also in cm/day). See eg Dillon and Rigler (1974), Vollenweider (1975), Ahlgren et al. (1998); and Harris (1994) for derivations and discussions of Australian applications. The values of v for the various water bodies determine the retention coefficients in relation to water flows – some generic values for northern hemisphere conditions are given in Table 1 below. In comparison to the data quoted above it was immediately clear that the Australian values must be very different. For example, values of v quoted below show that the apparent settling rate of P is always higher than that of N and that retention of N is rivers is quite small. Thus N:P ratios in northern hemisphere rivers are usually much greater that Redfield given (a) greater P removal than N and (b) high atmospheric loadings of N due to N and S deposition (acid rain, Holland et al. 1997). What the Australian data showed was the reverse – higher N removal in rivers than P (low DIN:DIP ratios) and N:P ratios frequently lower than Redfield. No combination of the values in Table 1 in a landscape model will produce the kinds of results observed in Australian catchments.

The combination of flow regulation, impoundment of rivers and removal of wetlands has had a major effect on the ecology of Australian rivers. Clearance and land use change, increased erosion and increased sodicity, have flipped many Australian rivers from clear and macrophyte dominated, to turbid and plankton dominated. These effects are probably no longer reversible without massive, and unrealistic, landscape rehabilitation. Landscape hysteresis is a phenomenon that requires careful management if we are to avoid even greater impacts from land use change. While the rivers have been largely lost, most Australian estuaries are not yet past the "critical load" point, further modification of catchments, flow regulation and urban developments are likely to see more and more of our estuaries go down the track of irreversible degradation.

Table 1. Generic values for Vollenweider's v for northern hemisphere wetlands, rivers and lakes (see Vollenweider 1968, 1969, 1975, 1976).

		Wetlands	rivers	Lakes
Vollenweider's v (cm/day) for:	Carbon	25		4
	Nitrogen	3	0.5	0.55
	Phosphorus	4	3-4	3.56
	Ammonia	4.5		

Pristine Australian catchments exported low amounts of N and P by world standards. This can be explained by the low nutrient status of many Australian soils, the low relief and the low rainfall. Overall catchment exports of N and P, even after modification, were found to be lower than elsewhere in the world – particularly the northern hemisphere – due to lower inputs from fertiliser and the atmosphere, lower population densities and lower runoff. The predominant N outputs for forested catchments are DON and this is only metabolised in the anoxic regions of monomictic (or meromictic) impoundments. The best predictors of TN exports from catchments and of TN in water samples were C exports and TOC in the water samples because the predominant form of N was DON, incorporating DOC. (For the Victorian data the highest correlation with TN was TOC, where N=83 and R^2 = 0.68). DON is largely unavailable for plant growth in aquatic systems – although some might be used in coastal marine waters (Seitzinger and Saunder 1997, Harris 1999a). Nitrate is not exported in large amounts from pristine catchments and is also in proportionally short supply in rivers and impoundments where the residence time of the water is long (qs is small). Nitrate disappears from inland river reaches through biological uptake and denitrification but is not consumed in coastal river systems where the water residence times are short.

Denitrification is both a function of the nitrate load and the water residence time (Figs 9, 10) and is increased by the presence of aquatic macrophytes which both take up N and stimulate the activity of biofilms around the roots and shoot bases. Evidence from the Port Phillip Bay Study (Harris et al. 1996) also hinted at a high Q_{10} (temperature response function) for denitrification, so that we might reasonably expect it to be more rapid in subtropical and warm temperate environments, compared to cooler temperate regions of the globe. To be an efficient sink for N, denitrification requires a carbon source (Brettar and Rheinheimer 1992) and adjacent oxic and anoxic zones – frequently found in estuarine sediments (Harris 1999a,c) and also in the margins of weir pools and impoundments with anoxic bottom waters.

Both denitrification and P release from sediments will be stimulated by soil sodicity and acidity (both increased by anthropogenic change) because of higher inputs of carbon and sulphur (Donnelly et al. 1997, Kleeberg 1998, Roden and Edmonds 1997). Whatever the cause – low inputs or rapid removal, or a combination of the two – the result was clear. DIN was frequently observed to be in limiting supply compared to P in Australian systems. Land use change coupled to flow regulation and impoundment of the rivers can therefore be a direct cause of the increased frequency of N-fixing cyanobacterial blooms (Harris 1999a).

The second reason for the low DIN:DIP ratios in Australian waters had much to do with the effects of erosion and gullying of acidic and sodic soils, the high clay loads in suspension and the buffering effects of the TOC, iron and bacterial interactions on P concentrations (Oliver et al.1993). Unlike the northern hemisphere, where particulate P settles out in lakes and rivers because of the higher divalent cation concentration and the higher ionic strengths of the waters, clay particles do not coagulate and settle out in our dilute, sodic Australian waters. (Unless the effects of ground waters, with higher ionic strength, are felt, Donnelly et al. 1997). Also unlike the northern hemisphere, most of the TP in Australian rivers comes from gullying and sub-soil erosion rather than from fertiliser use (Martin and McCulloch 1999, Olley and Caitcheon 2000). Thus there are correlations between TP and TSS in Australian waters – and TP concentrations are high (Oliver et al. 1993). Furthermore the DIP concentrations are well buffered through interactions with bacteria and the particle surfaces. The relationships between DIP and TP, with roughly constant DIP and %TP, is, by international standards, unusual. (Compare eg the data in Fig 23 with those in Janus and Vollenweider 1981.)

Thus, overall, and compared to studies in the northern hemisphere, Australian values for v must be largely reversed compared to those in Table 1. Land use change, impoundment and river regulation exacerbate this situation. The only N:P ratios that approach internationally comparable values are those from the Hawkesbury-Nepean River (Fig 24) where nitrate inputs are high from urban and agricultural inputs and residence times are short. P removal from wastewater treatment plants has also been in place for a number of years.

What has this work revealed in terms of robust indicators of water quality? While salinity (as EC units) is a robust indicator of hydrological change and reflects changes to the major ion chemistry of Australian waters, nutrients are more complex. As noted above most of the nutrient data collected are merely TN and TP data. TN and TP concentrations do increase as land is cleared for agriculture and urban development. Unfortunately these data, while necessary indicators of water quality and the risk of algal blooms, are not sufficient. There are differences in the TN and TP concentrations in Australian rivers and the ANZECC Guidelines were exceeded but most of the major differences between catchments and regions (eg inland vs coastal rivers) were found in the DIN and DIP data. It is well known that the DIN:DIP ratio is a good predictor of the risks of cyanobacterial blooms (Lean and Pick 1987). Harris (1996) discussed the use of nutrient ratios in the Australian context and also concluded that merely using TN and TP data was insufficient for a complete explanation.

The precise reasons for the geographical and catchment-by-catchment differences in the DIN and DIP data require further study, but the differences must lie in the catchment inputs, soil types, land uses and flow regimes. We know enough to make an initial analysis and explanation but more careful study is required, particularly the detailed geographical analyses of soil types and their linkages to land use and water quality. To fully understand these important interactions we must collect more complete water quality data sets. No analyses have been carried out here of temporal trends or of seasonal and flow related dynamics. Merely using annual, or longer term averages, has certainly lifted the lid on Pandora’s Box. Quite clearly the water quality data holdings of the State agencies are a veritable gold mine of information if biogeochemical analyses are undertaken. This paper is, for Australia, an unconventional approach to the data. It would be less unconventional if written in the Northern Hemisphere – nevertheless we have much to learn from the practices of other nations, many with much worse water quality problems than ourselves.

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