A procedure for evaluating the nutrient assimilative capacity of Darwin Harbour

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Executive Summary

- We advocate the application of nutrient assimilative capacity in Darwin Harbour within a preventative framework, with a capacity for forewarning. Current knowledge and understanding of nutrient dynamics in the harbour are insufficient to address the application of the concept fully. Without this knowledge, a nutrient loading capacity for the Harbour as a whole, and more importantly, specific parts of the harbour under immediate threat, cannot be properly evaluated.

- An overview of nutrient cycling in coastal waters has been presented, with *nutrient assimilative capacity* defined for this study as *the scope of the system to incorporate nutrients into living matter and sediments, so preventing build-up of nutrient concentrations in the water column, with two important provisos—that the nutrient assimilation process within the harbour does not lead to 1) loss of estuarine or coastal biodiversity, or 2) degradation of environmental services of the system*.

- In a review of nutrient cycling and distribution in Darwin Harbour, it is recorded that the water body is nitrogen limited (although phosphorus co-limitation has been noted in some instances). Nitrogen became the focus for our study.

- The dominant form of dissolved nitrogen is dissolved organic nitrogen, which is representative of a generally undisturbed system; this observation is corroborated by the low levels of chlorophyll *a* in the harbour. The top two primary producers have been identified as mangroves followed by phytoplankton in the water column. The order is reversed with respect to nitrogen and phosphorus demand (in effect, nutrient assimilation): phytoplankton and then mangroves, with other estimated uptakes assessed as trivial.

- Darwin Harbour is a net autotrophic system. Constraints on primary production (and hence, nutrient uptake) in the water column include light (attenuated by turbidity) and grazing. Both factors need to be characterised much more fully. The scope for pollutants (e.g. metals, organohalides, PAHs and TBT) to interfere with biological uptake of nutrients in Darwin Harbour is not known.

- Nutrient inputs into Darwin Harbour from terrestrial discharges (including human activities) have been well studied and documented; there are also predictions of likely increases with increased land clearing and urbanisation. It is concluded that these inputs will remain minor (<15% of total) compared to other known inputs, such as coastal sea waters and N fixation, but this does not preclude localised harm (a current example is Buffalo Creek). Further data gathering and research are needed to quantify definitively inputs from all other sources apart from surface, terrestrial diffuse and point-source discharges.

- Fates of nutrients are more poorly resolved than inputs. By analogy with studies elsewhere in tropical Australia (e.g. Great Barrier Reef), ultimate sinks for nitrogen are likely to be the atmosphere (via denitrification to N_2) with a minor loss to deep burial in sediments. Mangroves (and their ecosystems) are suggested to be effective intermediate repositories for nutrients.

- To apply the concept of a nutrient assimilative capacity in Darwin Harbour (within a preventative framework and having capacity for forewarning), multiple threshold indicators have been suggested to highlight changes in conditions. Recommended as these set of indicators are chlorophyll *a*, dissolved oxygen and as yet unspecified rates of reaction within the nitrogen cycle. The last indicator, or indicators, will be the outcome of research involving molecular biology techniques. Potential N-cycle indicators include rates of denitrification (possibly coupled with N fixation) and turnover rates for ammonia.

- Integral to the application of nutrient assimilative capacity as espoused in this report is the incorporation of the set of threshold indicators into a water quality model for scenario testing and vulnerability resolution. The RMA2/RMA11 package has already been used extensively for modelling hydrodynamics and sediment transport in Darwin Harbour. It has recently been enhanced to a full water quality model, and is the prime candidate for this work.

- Knowledge gaps were identified that are hampering effective evaluation of nutrient assimilative capacity. They were categorised under monitoring, process understanding and modelling. Aside from those covered in preceding dot points, other major deficiencies include: a need to establish the bioavailable fraction of dissolved organic nitrogen; quantification of heterotrophic bacterial activity; increased autonomous monitoring and across the full spectrum of harbour conditions; measurement of denitrification in sediments; assessment of the nutrient assimilation by sponges; improved characterisation of the underwater light environment; and focussed measurements in the outer harbour to improve model boundary conditions.

- Finally, the estimation of nutrient assimilative capacity of Darwin Harbour can be realised through a combination of observations, experimentation and modelling; a framework has been outlined. It is a process that would be used improperly if done only on a whole-of-harbour basis; its zoned application, and case by case, within the waterway guarantees more surely the integrity of ecological components (e.g. tidal creeks) of the full system.

1. Introduction

Nutrient assimilative capacity, drawing on the explicit technical meaning of the individual words, refers to the scope for nutrients (nutrient elements N, P, K, Si, Fe, etc.) to be incorporated into organic (cellular) compounds of living organisms. It is most commonly used when referring to the capacity of wetlands—natural (Correll et al. 1992) or constructed (Gray et al. 2000)—to filter out nutrients from waters in transit through the system. In this use, nutrients can be removed in living material (e.g. macrophytes and microalgae), detritus or the soils/sediments of the wetland.

When it comes to coastal water bodies, nutrient assimilative capacity is in practice defined by exception: when it is exceeded, in the view of the observer. Australian examples include, the increase of phytoplankton biomass at the expense of seagrass in Cockburn Sound, Western Australia (Pearce 1991), and when reviewing the effects of non-point sources more widely in coastal ecosystems (Gabric and Bell 1993).

The definition to be used in this report, in considering Darwin Harbour (a macrotidal estuarine system in the seasonally wet/dry tropics), is that nutrient assimilative capacity is the scope of the system to incorporate nutrients into living matter (mangroves, macrophytes, sponges, macroalgae, microalgae—pelagic or benthic, bacteria, etc., and the food webs supported by these primary producers) and sediments, so preventing build-up of nutrient concentrations in the water column. There are two important provisos: that the nutrient assimilation process within the harbour does not lead to 1) loss of estuarine or coastal biodiversity, or 2) degradation of environmental services of the system. An assessment of nutrient assimilative capacity can be applied to the entire water body or to individual compartments of it. The intent here will become clear through the report.

The domain of our study is the Greater Darwin Harbour as defined by the seaward boundary Charles Point to Gunn Point, which encompasses Port Darwin and Shoal Bay (Figure 1). This same boundary is used administratively, and in earlier reports considering its environmental quality and ecology (e.g. Padovan 2003, McKinnon et al. 2006). The macrotidal harbour has a maximum tidal amplitude of 7.8 m (mean spring amplitude: 5.5 m; mean neap amplitude: 1.9 m). Its surface area is 1220 km^2 at the highest astronomical tide and 660 km^2 at the lowest astronomical tide, which compares with a relatively small catchment area of 2010 km^2 (Skinner et al. 2009), of which ~7% of total system area is mangroves fringing the water body. It is a shallow estuary with water depth of 20–30 m in the main channel at the mouth of the Darwin Harbour, a maximum depth of ~40 m within the harbour, decreasing to 5–10 m in its arms. The mean annual rainfall is 1731 mm; most falls between December and March in the wet season (~80%; Bureau of Meteorology http://www.bom.gov.au/climate/data/index.shtml (accessed 24 Aug 2013); Darwin Airport). During the dry season (May–September), the rivers feeding Darwin Harbour (Blackmore River into Middle Arm, Elizabeth River into East Arm, and Howard River into Shoal Bay) cease to flow, apart from a small residual flow from aquifer-fed springs into the Blackmore River. The harbour is a stratified estuary (with fresher surface waters) for a few days to a few weeks at a time in the upper estuary during the wet season, depending on rainfall (Williams et al. 2006, Drewry et al. 2010b). At all other times, it is a vertically well-mixed estuary (uniform salinity top to bottom). During the dry season, the harbour becomes an inverse estuary with hypersaline water (exceeding seawater salinity) formed in its landward arms as a result of evaporation.

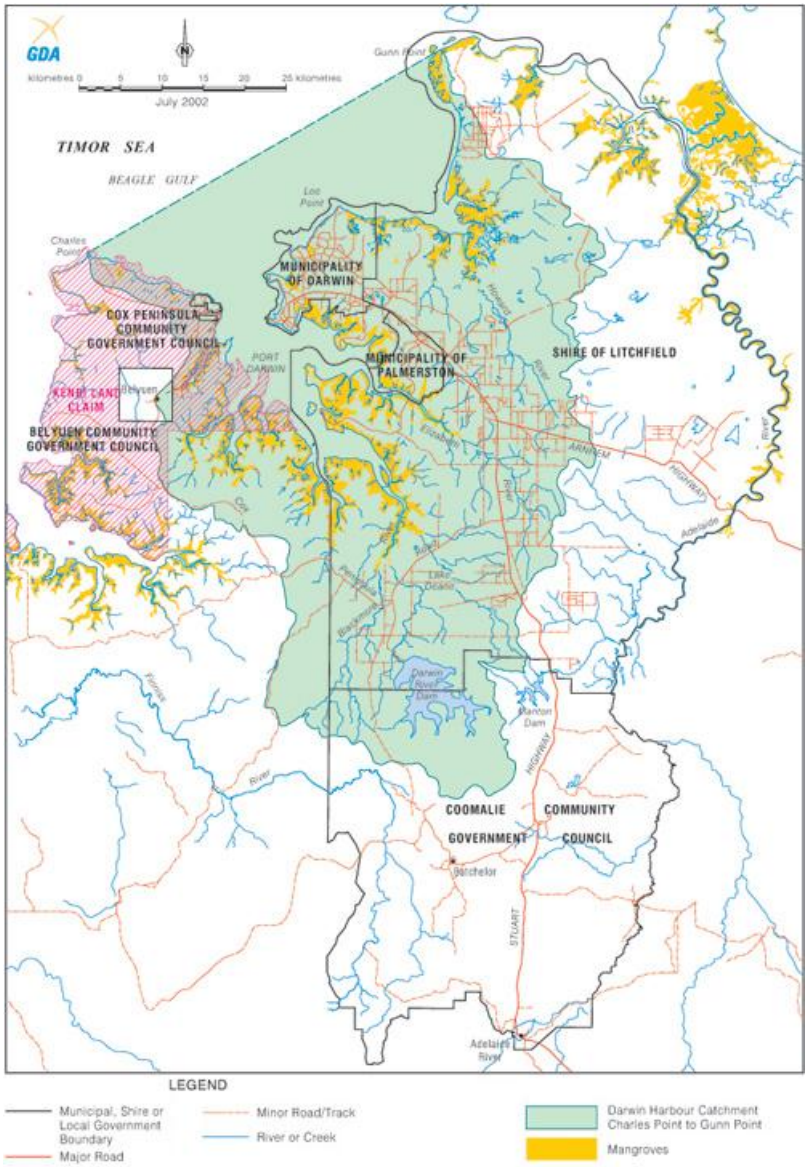

Figure 1. Map of Darwin Harbour and catchment, along with administrative boundaries (Source: http://www.lrm.nt.gov.au/water/dhac/map).

The historic condition of Darwin Harbour, which persists in the main water body to this day, is low concentrations of chlorophyll *a* (Chl *a* – a measure of phytoplankton density) and dissolved nutrients, but with high concentrations of suspended particulate matter (or 'suspended solids') (Padovan 1997, 2003). The former results from oligotrophic, tropical oceanic waters from the Timor and Arafura Seas mixing with the run-off from ancient, weathered catchments of Northern Australia; the latter ensues from the large tides remobilising fine sediments from the shallow harbour floor, and especially from the intertidal mudflats. What is confusing is that measures of system productivity (e.g. net primary production of 400 g C m^{-2} y^{-1}) suggest that the harbour is overly productive or eutrophic. This productivity is attributed to the mangroves, inhabiting at least two-thirds of the foreshore, and their ecosystem (McKinnon et al. 2006, Burford et al. 2008).

This desktop study forms part of the Darwin Harbour Water Quality Protection Plan (WQPP) project and conforms to a priority of the plan to protect Darwin Harbour waterways from excessive nutrient inputs. We outline a mechanism for evaluating a nutrient

assimilative capacity for the water body as a whole, but with the flexibility to be applied to a compartment or sub-region of the harbour.

1.1. Objectives of Investigation

The goals of this study are:

1) To present what is known currently of the status and function of Darwin Harbour in regard to nutrient loads and the processing of these;
2) To outline how to address the question of nutrient assimilative capacity of the Harbour, and what further knowledge is needed to achieve it;
3) To identify how to tackle the knowledge gaps and recommend a priority for their resolution.

These goals will be realised through a series of tasks as follows:

a) literature review of nutrient distribution and cycling in Darwin Harbour, within the context of the system's ecology; this will also include current nutrient loads of nutrients (from catchments and WWTPs)—dissolved and particulate—and the different fates of these forms;
b) appraisal of the available nutrient data: its coverage, accessibility, and relevance in forming an assessment of nutrient assimilative capacity;
c) consideration of different paradigms for identifying exceedance of assimilative capacity of Darwin Harbour for nutrients, and how related thresholds might be obtained;
d) assessment of a model approach that will canvass such matters as scenario testing, zonal assimilative capacities and identification of sensitive areas (hot spots), and optimisation of observational/monitoring programs;
e) as *key knowledge areas*, elaborate on the following: nutrient speciation and distribution; critical nutrient ratios (N:P, etc.) and their effect on communities of micro-organisms; nutrient sources/sinks and cycling, and associated harbour compartmentalisation; light limitation of primary production and interplay with other drivers; model underpinning—relevant chemical thermodynamics and kinetics, and 'decay coefficients';
f) as *information requirements (specific to Darwin Harbour)*, look into eutrophication and toxicity (e.g. ammonia about WWTP outfalls) testing; and laboratory experiments to determine threshold levels/ trigger values that come out of earlier stages of this study;
g) evaluation of the preceding tasks to reveal the knowledge/information gaps (available resources against needs); and
h) determine the priority for filling the knowledge/information gaps, and formulate in a set of recommendations

2. Nutrient distribution and cycling in Darwin Harbour, and the broader system ecology—a review

2.1. Nutrient cycling—an introduction

An array of nutrients is required for plant growth in estuarine and marine waters; from the generally abundant oxygen and carbon to the trace amounts of micronutrients, such as cobalt, iodine and zinc (Morel et al. 2003, Libes 2009). The macronutrients nitrogen and phosphorus are vital to marine plants, whether mangroves or single-celled phytoplankton; a third macronutrient silicon is essential for planktonic diatoms.

Nitrogen cycle

The marine nitrogen cycle is a sequence of interconversions of different forms (or species) of nitrogen that is facilitated by biological activity, particularly that of microbiota (Cabello et al. 2004, Brandes et al. 2007; Figure 2). The key entry into the cycle is the conversion of inert nitrogen gas in the atmosphere to ammonia (predominantly ammonium ion NH_4^+ in natural waters); this step is accomplished by nitrogen-fixers, unicellular algal species, such as *Trichodesmium,* other diazotrophs found in the microphytobenthos (MPB) and archaea. Ammonia is converted by a host of nitrifying bacteria to nitrate. Ammonia and nitrate are pivotal (Zehr and Ward 2002), because they are taken up by cells for biosynthesis of proteins, nucleic acids and other nitrogen compounds. If these bioavailable N species are not incorporated into living cells, they are converted back to nitrogen gas (via several N intermediates) by competing denitrifying bacteria or archaea to complete the loop.

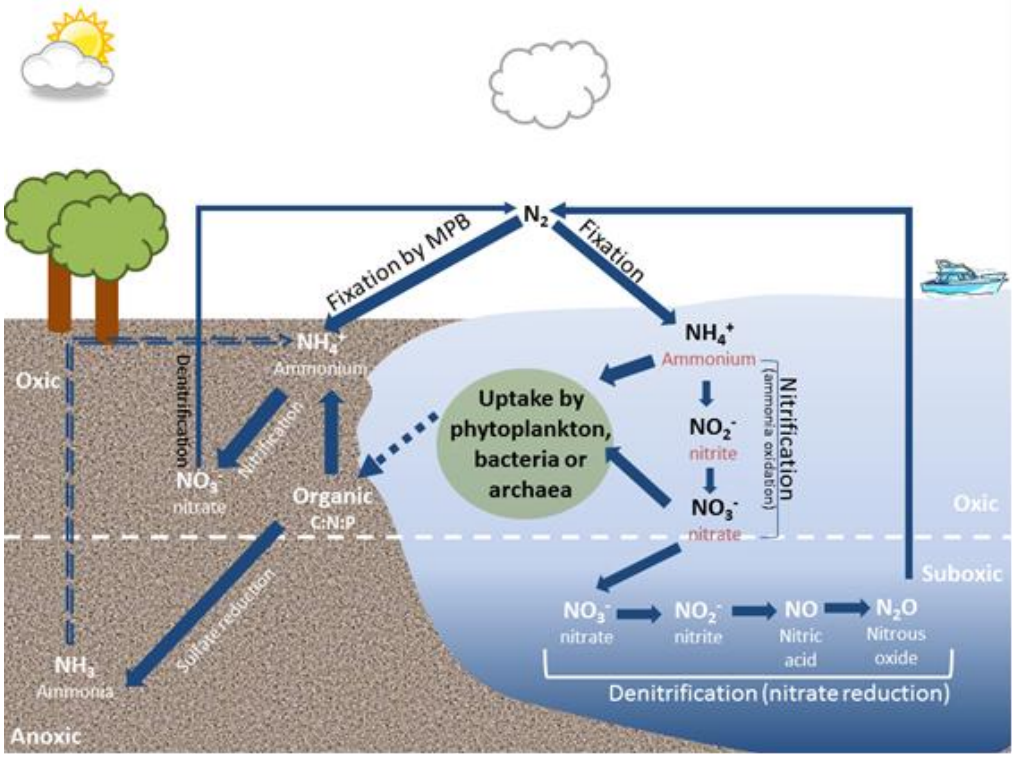

Figure 2. The nitrogen cycle in the coastal marine environment. MPB: microphytobenthos

Dissolved organic nitrogen (DON) forms a side branch to the N cycle (Figure 3). It is released into natural waters by living cells, and also on their death. DON in estuarine and coastal waters is a complex spectrum of compounds resulting from local and remote (e.g. terrestrial

run-off) sources (Bronk, 2002); it is further modified by photochemical reactions and reworked by biogeochemical processes. Macromolecular forms of DON (e.g. humic and fulvic acids) can be quite inert and persistent, but their ultimate pathways are either aggregation to particulate organic N (PON) and depositing in sediments, or microbial decomposition to bioavailable forms of DON and remineralisation to ammonia, and thus, returning to the central N cycle.

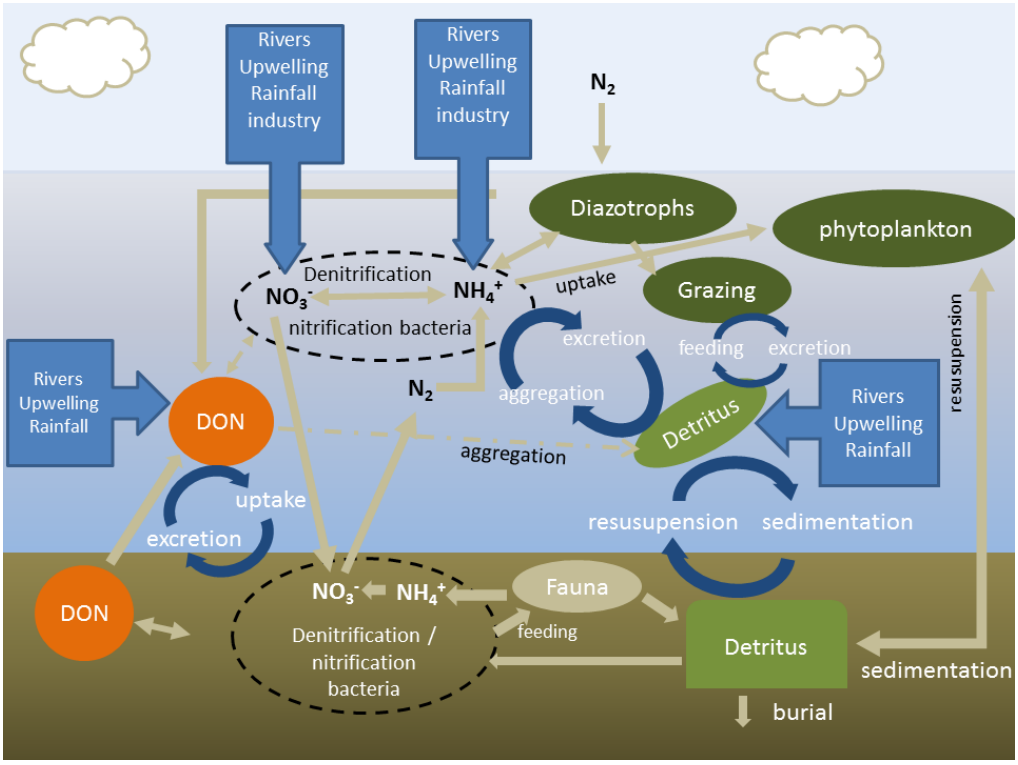

Figure 3. Sources of nitrogen pools and their entry into the nitrogen cycle (modified from Furnas et al. 2011). DON: dissolved organic nitrogen; the green ellipses also represent particulate organic nitrogen.

Traditionally it was thought that inorganic nitrogen was only assimilated by eukaryotic plankton and that primary role of heterotrophic bacteria in the N cycle was the release of ammonia during the decomposition of organic matter so it was available for phytoplankton (Zehr and Ward 2002). It is now known that species of heterotrophic bacteria are also capable of assimilating nitrogen. For example, studies of heterotrophic bacteria in Barents Sea showed that their uptake of dissolved inorganic nitrogen (17–36% of nitrate and 12–40% of ammonia) was appreciable in polar oceans (Allen et al. 2002); a similar prominence is inferred for shelf waters of the Great Barrier Reef (Furnas et al. 2011). Heterotrophs can be competing with phytoplankton for ammonia, regenerating ammonia through decomposition or simultaneously doing both (Zehr and Ward 2002).

Nitrogen cycling in sediments remains essentially unaltered from the water column, but it is compressed in the vertical scale, constrained by the supply of dissolved oxygen, and modified by heterogeneous (viz. particle-surface) reactions and higher densities of microbes. Important characteristics to note are that denitrifiers are restricted by redox potential, competition for nitrate with other bacteria, and supply of organic matter (Alongi 1988, Rivera-Monroy & Twilley 1996). Oscillation between oxic and anoxic conditions in surface sediments can promote denitrification (Laverock et al. 2010, Devries et al. 2012). Whilst, increasing supply of

organic matter can switch coastal sediments from net nitrogen fixation to net denitrification (Fulweiler et al. 2007).

High rates of denitrification (compared to opposing reactions) result in its dominance in coastal waters; this is reasoned as the cause of N being limited almost universally in estuarine and coastal waters (Harris 2001a, Howarth et al. 2011; and see Section 2.2 below). A recent review by Burgin and Hamilton (2007) contends that perhaps too much emphasis has been placed on respiratory denitrification as the removal process for nitrate. They have postulated five other pathways (or variations of pathway) that remove it. Most of the five have N_2 either as the end-product or an option, but some end up with bioavailable ammonia. One of the alternative nitrogen pathways is anammox, which has been identified as possibly the main N cycling pathways in suboxic environments (Zehr and Kudela 2011).

Phosphorus cycle

The central inorganic and bioavailable form of phosphorus is phosphate (Figure 4; represented as PO_4, and analytically determined as molybdate-reactive P). Like the N cycle, the P cycle is strongly regulated by the activity of micro-organisms (Dyhrman et al. 2007), but it differs from

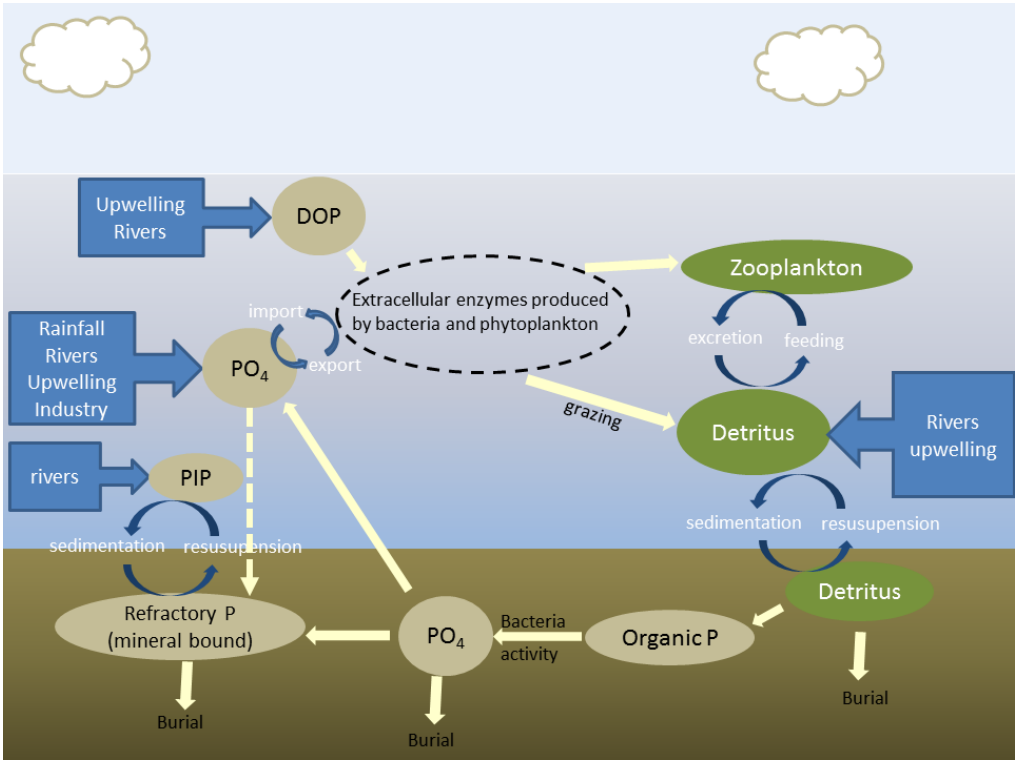

Figure 4. Phosphorus cycling in marine environment. PIP – Particulate inorganic phosphate, DOP – Dissolved organic phosphate.

N in also being highly *particle-reactive*. Geochemical processes of adsorption and desorption on mineral surfaces[1] (e.g. hydrous oxides of Fe, Mn, Al, clays, etc.)—either as suspended particles or sediment surfaces—determine its concentration in solution, and hence, its bioavailability (Paytan & McLaughlin 2007). Phosphate is taken up within cells and converted to dissolved organic P (DOP; e.g. phospholipids, phytin, nucleic acids). When released back into solution,

[1] In reality, these will not be pure phases, but particles composed of minerals, organic matter among which are rich populations of micro-organisms (Cowan & Bruland 1985, Mackey & Zirino 1994)

DOP can be remineralised by microbial activity (Thingstad et al. 1993; e.g. extracellular enzymes, such as alkaline phosphates) or become adsorbed to particle surfaces.

Other forms of phosphorus in the marine environment include inorganic polyphosphates (refractory polymeric forms of phosphate) and P associated with various minerals that contribute to the particulate inorganic P (PIP) phase (Benitez-Nelson 2000), Paytan & McLaughlin 2007). PIP is introduced by terrestrial run-off, but it is also produced authigenically in seawaters. If not remineralised by biological processes to return into the marine P cycle, PIP is buried in sediments (e.g. phosphorite deposits).

In sediments, bacteria actively decompose organic P to phosphate (Gächter and Meyer 1993), but the latter is only released to sediment porewaters if bacterial nutritional requirements are met (Thingstad et al. 1993). Even then, the availability of phosphate is not assured, it is influenced by redox potential (P release from hydrous Fe and Mn oxides under reducing conditions: suboxic to anoxic), sorption to clay particles, humic acids, bioturbation, mobilisation by macrophytes, and physical processes, such as resuspension and wave pumping (Paytan and McLaughlin 2007**)**.

Factors effecting nutrient cycling

Our consideration of the N and P cycles here has been necessarily brief, and has not elaborated the full complexity of them. We emphasise that the N and P cycles do not exist in isolation, they interact closely with one another (e.g. they are closely linked intracellularly in such as nucleic acids and nucleoside triphosphates), and they are modulated by other elements cycles, particularly carbon and sulphur. An example has already been provided above of a link between the C and N cycles: denitrifying bacteria couple the conversion of nitrate (or N intermediates) to N_2 with decomposition of organic matter. Another example is carbon availability (a combination of concentration and form of organic carbon) being inversely related to the rate of nitrification by sediment bacteria (Strauss and Lamberti 2000). It has been proposed that the decline in nitrification arises from organic carbon stimulating non-nitrifying bacteria, which are then able to outcompete nitrifying bacteria. Some sedimentary bacteria species (e.g. *Roseobacter denitrificans*), capable of both denitrification and nitrogen fixation, also use sulfate as an electron acceptor (Fulweiler et al. 2013). The ability of these bacteria species to switch between N and S as energy sources is but one example of why both cycles are intimately linked in sediments. The third marine macronutrient Si has not been discussed above, but its cycling is also entwined with N and P. It is crucial to the siliceous microalgae diatoms, but also to other life forms, such as Radiolarians and sponges.

The micronutrient metals (Fe, Mn, Zn, Co, Cu, etc.) are important as cofactors in many enzymes. Recent studies have shown that bacterial communities in sediments of tropical areas (Cornall et al. 2012) are influenced by bioavailable metal concentrations. Insufficiency of essential trace metals causes activities of enzymes to be depressed, if not inactivated, and certain microbial taxa can be become nutrient limited. However, if the situation tips over into excess concentrations of metals, as in contaminated waterways, other metals can become enzyme inhibitors or even cause toxic effects. Other organic contaminants, such as organohalides, PAHs, triazine compounds, can also have detrimental consequences for nutrient cycling and uptake by harming communities of micro-organisms (Koelmans et al. 2001).

Aside from nutrients (and their antagonists), the availability of light—or strictly its intensity and quality—is the other primary factor in the productivity of phytoplankton (Kirk 2011). Turbidity from total suspended sediment and coloured dissolved organic matter (CDOM – e.g. humic substances) is the main factor attenuating light in Darwin Harbour. There is

currently a lack of information on the underwater light environment (Mobley 1994) that characterises the surface waters of Darwin Harbour and its neighbouring coastal zone. We can surmise the effects of turbidity on light (e.g. photosynthetically available radiation; PAR) and the ensuing effects on primary production and nutrient cycling from studies in other parts of the world. For example, Pratt et al. (2013) have shown that increasing suspended solids concentration constrained the primary productivity of MPB (three-fold reduction) and enhanced the efflux of nutrients (e.g. four-fold increase in ammonia release) from sediments in benthic chambers. Studies of the influence of light (PAR) in the freshwater tidal zone of a mesotidal, turbid estuary (Domingues et al. 2011) revealed that diatoms were the most light limited, while cyanobacteria were the only taxa capable of acclimating to the low light. Wan et al. (2013) incorporated a light attenuation algorithm into a physical–biogeochemical coupled model and demonstrated improved results for nutrients, chlorophyll concentrations, and primary production.

Other physical (e.g. salinity, turbulence, sediment grain-size and porosity), chemical (e.g. dissolved oxygen and pH) and biological (e.g. grazing pressure) conditions also influence nutrient cycling and assimilation. These will be highlighted as necessary later in the report when considering the environment of Darwin Harbour. Subtle changes in microbial community structure, possibly resulting from physico-chemical factors but also arising from within-community interactions (bloom progressions, grazing effects, even quorum sensing) also alter nutrient biogeochemistry. For example, a transition in the class of phytoplankton from diatoms to cyanobacteria (e.g. Cook et al. 2004) can change the status of surface coastal seawaters from N limited to N replete.

2.2. Nutrient distribution and cycling within Darwin Harbour

The distribution and biogeochemical cycling of nutrients is considered here from the seaward boundary of Darwin Harbour to the tidal limit in the upper reaches of its arms. It also encompasses the zone of maximum inundation under a spring high tide, which draws in the fringing vegetation, such as mangroves.

The relative proportions of macronutrients in marine organic matter are remarkably uniform worldwide (Redfield Ratio, C:N:P 106:16:1 by atomic ratio), and this is fundamentally a result of biological assimilation (Redfield 1958). Since the dissolved N:P ratio in Darwin Harbour waters is about half the expected 16:1 (McKinnon et al. 2006) and that N (added in ammonium form) was growth stimulating and not P (added as phosphate) for incubations of the same marine harbour waters (Burford et al. 2008), it is N that is regarded as the *limiting nutrient*. This condition is common in Australian estuaries (Harris 2001a). P co-limitation is possible in upstream, brackish waters, as observed by Burford et al. (2008) for Darwin Harbour surface waters in February (wet season outflow).

Nitrogen is rightfully the focus of our study, because its addition will have the greatest effect on the trophic state of Darwin Harbour. Other nutrients will not be totally neglected, because they are interconnected with the N cycle and primary production (see above), and they might serve as useful environmental-quality indicators.

Nutrient distributions and other relevant environmental variables

Total N in Darwin Harbour is generally in the range 100–600 µg N/L and uncorrelated with tide, season or location; the bulk is dissolved organic N (DON) (Padovan 2003; Dostine 2013). The predominance of DON is indicative of an estuarine system that remains relatively unmodified from historical conditions (Harris 2001b). Dissolved inorganic N (DIN, the sum of nitrate, nitrite and ammonia) is between 3 and 12% of the total N concentration, and its constituents NO_x (the sum of nitrate, nitrite) and ammonia almost invariably meet the water quality objective of <20 µg N/L (Report Cards [2]2009–2012). DIN comprises bioavailable forms of N: NO_x varies with season, peaking in the wet season. Ammonia is generally at low and uniform levels (~10 µg N/L) throughout the year (Padovan 2003), but it increases in the vicinity of waste-water treatment plants (WWTPs; Report Cards 2009–2012) and possibly with remineralisation in low-oxygen conditions in river arms. An unresolved question is how much of the dominant DON fraction is bioavailable.

Phosphorus, as Total P, varies within a small range 10–30 µg P/L in Darwin Harbour. It is generally uniform down the water column, but is a function of turbidity and so varies with tide and location (Padovan 2003). Total P is also strongly sourced from WWTPs (Report Cards 2010). Between 20 and 50% of the P is in the bioavailable form, dissolved inorganic P (DIP).

Limited data is available for silicon, coming from a year-long study (Oct 1990–Nov 1991; Padovan 1997). Dissolved molybdate-reactive silicon (hereafter referred to as silicic acid) varied between usually 300 and 600 µg Si/L in the dry season in the harbour. During the wet season peak concentrations increased in the middle harbour (900–1100 µg Si/L), but the peaks remained lower toward the mouth (600–800 µg Si/L). Silicic acid concentrations were not measured in the riverine arms, but it is likely that they were much higher, because concentrations are mentioned of 10 mg Si/L "in rivers adjacent to the Darwin Harbour

[2] Darwin Harbour Region Report Cards are a publicly available, annual record of environmental quality of the Darwin Harbour Region available at <www.lrm.nt.gov.au/water/dhac/reportcards>.

catchment [cites WRD records]". An inverse relationship for Si with salinity is expected (Burton et al. 1970).

Dissolved oxygen (DO) concentrations play a decisive part in all aspects of biological nutrient processing, and as recounted above, the influence extends beyond to chemical redox control (with DO as a master variable) of phosphate release from mineral phases. The water column in the main body of Darwin Harbour is well oxygenated (65–100% saturation) (Padovan 1997, Report Cards 2009–10). Levels of saturation decline in the arms of the Harbour (50–85%; e.g. estuaries of Elizabeth and Blackmore Rivers—see Dostine 2013 for former). Greater oxygen demand from organic matter, originating from the mangrove forests along the banks, is suggested as a reason (Padovan 2003). DO concentrations also cycle with the tides to a minimum at low tide with outflow from the arms, and are restored on the incoming tides with well oxygenated coastal seawaters.

Turbidity is proportional to the suspended solids concentration, which has an influence on nutrient biogeochemistry by not only affecting light quality, and therefore photosynthesis, but also by providing particle surfaces for adsorption/desorption reactions and microbial colonisation. Darwin Harbour turbidity varies from 1 to >30 NTU (Padovan 1997, Padovan 2003, Report Cards 2009-10). It is variable over time, location and with depth. This variability is attributed to fluctuation in tidal currents during a day and from neaps to springs; it is also affected by characteristics of the sediments (grain size, cohesiveness) over which they flow and water depth. Increased turbidity in the wet season has been attributed to wash-off from catchment soils, but the magnitude is not great (means: 4 & 12 NTU, Dry to Wet). However, other mechanisms, such as the dispersion of mangrove sediments associated with brackish waters (originating from freshwater inflow) may also contribute to upper estuarine high turbidity in the wet season.

Chlorophyll *a* (Chl *a*) gives a measure of phytoplankton biomass. Its range is <0.5–3.0 µg/L for data over time in the main body of Darwin Harbour (Padovan 1997, McKinnon et al. 2006, Report cards 2009–12). During 2004, McKinnon et al. (2006) observed that harbour-wide mean concentrations were uniformly low throughout the year (wet season, 0.77 µg L^{-1}; dry season, 0.89 µg L^{-1}). Peaks of up to 8 µg/L Chl *a* have been observed in harbour arms, but are typically 25% of that concentration; however, Chl *a* levels can be an order of magnitude higher in tidal creeks affected by WWTP discharges. Chl *a* is reported not to vary seasonally but episodically through the year (Padovan 1997).

Other water-column data relevant to Darwin Harbour, obtained in 2003 (McKinnon et al. 2006), are presented in Table 1.

Table 1. Means and ranges of water column variables in wet and dry seasons, 2003 (McKinnon et al. 2006). The data represent means ± standard deviation of near surface and near bottom water samples at nine stations throughout Darwin Harbour.

	Feb 2003 (Wet)	**June 2003 (Dry)**
Elizabeth River flow, February (ML d^{-1})	1693 ± 1823 163–8901	0 0
Blackmore River flow February (ML d^{-1})	2356 ± 2319 189–7883	0 0
Temperature	28.82 ± 0.60 26.81–29.71	25.11 ± 0.31 24.38–25.62
Salinity	23.47 ± 9.71 0.09–35.61	34.29 ± 1.67 28.52–35.61
Suspended solids (mg L^{-1})	19.93 ± 18.94	5.62 ± 2.30
pH	8.12 ± 0.40 7.36–8.49	8.05 ± 0.16 7.78–8.24
Dissolved oxygen (mg L^{-1})	5.85 ± 0.42 5.52–6.68	6.03 ± 0.35 5.35–6.55
Ammonium, NH_4 (µM)	0.90 ± 0.79 0.26–3.46	0.27 ± 0.20 0.07–0.77
Nitrite, NO_2 (µM)	0.53 ± 0.16 0.18–0.74	0.08 ± 0.13 0.01–0.56
Nitrate, NO_3 (µM)	1.54 ± 0.63 0.07–2.46	0.29 ± 0.53 0.04–2.30
Dissolved organic nitrogen, DON (µM)	11.43 ± 4.10 6.14–24.19	10.41 ± 2.81 5.43–19.31
Total dissolved nitrogen, (µM)	14.41 ± 4.09 9.03–26.93	11.06 ± 3.06 5.78–19.63
Particulate nitrogen, PN (µM)	2.35 ± 1.34 1.14–6.22	1.31 ± 0.53 0.72–2.9
Phosphate, PO_4 (µM)	0.38 ± 0.10 0.15–0.58	0.35 ± 0.11 0.22–0.68
Dissolved organic phosphorus, DOP (µM)	2.00 ± 1.26 0.37–5.0	0.51 ± 0.30 0.18–1.86
Total dissolved phosphorus, (µM)	2.38 ± 1.25 0.66–5.27	0.86 ± 0.32 0.47–2.08
Particulate phosphorus, PP (µM)	0.24 0.15–0.35	0.13 0.08–0.35
Silicate, SiO_4 (µM)	16.42 ± 10.70 5.79–36.05	12.02 ± 13.28 4.89–56.49
Chlorophyll *a*, Chl *a* (µg L^{-1})	0.77 ± 0.42 0.12–1.99	0.89 ± 0.57 0.41–2.55
>10 µm Chlorophyll *a*, (µg L^{-1})	0.17 ± 0.43 0.01–0.47	0.35 ± 0.25 0.15–0.97
Heterotrophic bacteria (*1000)	153.71 ± 98.45 48.85–355.1	106.49 ± 57.76 42.65–236.07
Zooplankton biomass (mg m^{-3})	96.35 ± 158.90 27.14–674.61	62.13 ± 30.07 23.2–106.02
Zooplankton abundance (*1000)	33.49 ± 17.24 20.42–72.16	41.08 ± 37.71 13.09–136.20

Nutrient cycling in mangroves

Our discussion of nutrient cycling in Darwin Harbour begins with the mangroves, moves to the intertidal mudflats and adjacent subtidal sediments, and finishes with the pelagic system in the harbour waters.

Mangroves occupy two-thirds of Darwin Harbour's foreshore (204 km^2; Brocklehurst & Edmeades 1996) and are one of the main contributors to nutrient cycling in Darwin Harbour (McKinnon et al. 2006). These forests are diverse in having 36 species—half of the world's mangrove inventory. Knowledge of mangroves in the harbour has been reviewed by McGuinness (2003).

Mangrove systems are important barriers structurally, but also to pollutants (such as nutrients and metals) entering the harbour because they act as filtering systems (Alongi 2009). They are also one of the most productive ecosystems globally, with an average productivity of 2,500 mg C m^{-2}, often four-fold greater than adjacent coastal waters (Jennerjahn & Ittekkot 2002). They are the most productive component of Darwin Harbour (1,609,220 t C y^{-1}; Burford et al. 2008). The movement of organic matter and nutrients in and out of the forests is driven by tidal exchange. Originally, it was thought there was a large efflux of organic matter out of these systems into the tidal creeks and coastal waters beyond (Robertson & Duke 1990), but the current view is that they are more parsimonious with export of carbon (Bouillon et al. 2008), and almost certainly other nutrients. Alongi and McKinnon (2005) observe that although particulate matter export is significant, it is refractory aged litter that is nutritionally very poor with an average C:N ratio of 52:1.

Burford et al. (2008) have estimated a nutrient demand for mangroves of 12,750 t N y^{-1} and 1,380 t P y^{-1} from the data of McKinnon et al. (2006). This places mangroves second to only pelagic phytoplankton for nutrient uptake in Darwin Harbour (see below).

Based on knowledge of other tropical ecosystems, we can infer properties of mangrove systems in Darwin Harbour:

- the bulk of the N and P required by mangroves in Darwin Harbour will be provided by heterotrophic microbial activity in the mangrove sediment, with possibly the mangroves stimulating the bacteria by root excretion of organic matter (Nedwell et al. 1994);
- aside from microbial aerobic respiration and anaerobic sulphate reduction, recent evidence also supports iron respiration in the sediments (Kristensen et al. 2008);
- the mangrove trees themselves harbour nitrogen-fixing bacteria (in their bark – Uchino et al. 1984, and in their pneumatophores – Lugomela & Bergman 2002), and so have a direct source of supplementary DIN;
- efflux of carbon and nitrogen out of these systems will be limited owing to the sediment characteristics (reducing redox potentials and fine grain size) and microbial activity—this is supported by stable isotope studies (e.g. Bouillon et al. 2008);
- tannins released from the trees are important in regulating DON, particularly its retention in the system (Maie et al. 2008, Alongi 2009);
- other than mangrove litter, the other important autochthonous carbon source (and consumer of nutrients) are benthic microalgae (Kristensen et al. 2008)

Nutrient cycling in mud flats and sediments

Tidal mud flats are primary depositional sites in macrotidal systems, such as Darwin Harbour, for organic carbon exported from the catchment, other anthropogenic sources and whatever

escapes mangroves. The high POC concentrations on the mudflats are augmented by in-situ benthic microalgal production. Even though the intertidal mudflats (557. 3km^2, 226,210 t C y^{-1}) and the subtidal mudflats (660 km^2, 227,800 t C y^{-1}) were individually double and more the area of mangrove forests, they were a fraction of the productivity of the last (Burford et al. 2008). They were both measured at ~14% of mangrove gross productivity.

Nevertheless, the high organic C load on both types of mudflat, from allochthonous and autochthonous sources, has a high nutrient demand. This respiratory requirement for N (by heterotrophic bacteria) would appear to be met by the highest rates of N-fixation observed in the harbour (intertidal mudflats, 2733 t N y^{-1}; subtidal mudflats, 1956 t N y^{-1} – Burford et al. 2008), because N import to and export from the mudflats were negligible, although we do not know what amount of recycled N became available from diagenesis deeper in the sediments.

Studies from an intertidal mudflat in a temperate climate (Huon Estuary, Tasmania; Cook et al. 2004) suggest that organic C from terrestrial run-off is refractory. That which is produced in excess by MPB when living (e.g. exopolysaccharides when nutrient limited) or subsequently from dead cells of MPB and pelagic phytoplankton is much more labile, and available to heterotrophic organisms (Goto et al. 1999). We do not know if the same source distinction as to the nature of organic carbon applies under tropical conditions.

Rates of denitrification have not been measured anywhere in Darwin Harbour, apart from a handful of measurements in a couple of tidal creeks (see below). This is a critical deficiency. As we have recounted above in discussing the N cycle generally, it is the concentration of organic matter that can determine whether nitrogen fixers (low C) are active, or if they are supplanted by denitrifiers (high C) (Fulweiler et al. 2007). The productivity of nitrogen fixers on harbour mudflats—intertidal or subtidal—suggests that much of the organic carbon in mudflat sediments is refractory (i.e. not bioavailable, or its degradation by possibly a specialised group of microbes is very slow).

The availability of nitrate in sedimentary environments suitable for denitrifying bacteria can be another constraint on their activity. This hindrance might ensue from competition for nitrate between denitrifiers and decomposing bacteria, with the latter group immobilising or shielding the nitrate for their own use (Alongi 1988, Rivera-Monroy & Twilley 1996).

In coastal sediments, especially intertidal sediments, coupled nitrification/denitrification (i.e. oxidation of ammonia to nitrate, then stepwise reduction to N_2 via N_2O) is the dominant denitrification process. The cycle of tidal inundation and exposure imposes a sedimentary oscillation between oxic–suboxic/anoxic conditions, suiting the different redox potentials required by nitrifiers and denitrifiers (Rivera-Monroy & Twilley 1996). Such conditions should be optimal in mangrove sediments and their adjacent intertidal mudflats. Although the mangroves might be proficient at preventing loss of essential nutrients in dissolved form to nearby aquatic environments, they cannot prevent loss of some nitrogen to the atmosphere (Alongi 2009).

A comparison of the nutrient cycling in intertidal mud flats of two tidal creeks (Myrmidon and Buffalo Creeks) that receive elevated levels of nutrients from WWTPs is instructive about overloading the harbour's sensitive receiving environments. Based on sediment nutrient flux, the nutrient assimilation capacity has been exceeded in Buffalo Creek but not at Myrmidon Creek (Burford et al. 2012, Smith et al. 2012). The assimilation capacity of the former's sediments has been swamped so that N and P build up in the water column. The critical factor for two creeks receiving similar nutrient loadings seems to be flushing time, determined by

tidal exchange: [3], 1.6–4.8 d (Buffalo Creek) compared with 0.3–0.6 d (Myrmidon Creek) (Burford et al. 2012). In comparing the contaminated Myrmidon Creek with uncontaminated Reference Creek, Smith et al. (2012), found confirmation that Myrmidon Creek's sediments were in functional condition; it and Reference Creek had similar rates of benthic respiration (65–92 mmol C m^{-2} d^{-1}), and were comparable with Darwin Harbour generally (65–74 mmol C m^{-2} d^{-1}). It was only Buffalo Creek that was anomalous (271–391 C m^{-2} d^{-1}).

In Reference and Myrmidon Creeks, denitrification was consistently high (5.50–6.83 mmol N m^{-2} day^{-1}), while at Buffalo Creek, it was low and variable (Smith et al. 2012; K Gibb, personal comm., reports denitrification completely shut down in some areas of Buffalo Creek). Denitrification efficiency was high (83–97%) at the former two creeks, but was <10% at Buffalo Creek.

Nutrient cycling in the water column

Despite the sometimes high turbidity of Darwin Harbour seawaters that often limit the euphotic zone to the top 10 m (Padovan 1997), it is a net autotrophic system (mean P_G/R 2.1 observed for studies in 2004 and 2006; Burford et al. 2008). Primary production is high in the thin surface layer; highest surprisingly in the wet season (mean net production of 2.2 ± 0.8 g C m^{-2} d^{-1}; c.f. dry season, 1.0 ± 0.2 g C m^{-2} d^{-1}; McKinnon et al. 2006). Gross pelagic production at 395,170 t C y^{-1} is second only to the mangrove production around the perimeter of the harbour (Burford et al. 2008). In terms of nutrient demand (56,000 t N y^{-1} and 3300 t P y^{-1}), pelagic phytoplankton are the dominant mechanism for uptake of N and P throughout the harbour.

The high production in Darwin Harbour surface waters is not translated to high microalgal biomass. Mean harbour-wide Chl *a* concentrations are likely to be < 4µg/L Fortune (2010) or even <1.0 µg/L, regardless of season (see above and Table 1). Horizontal distribution of biomass is influenced by season; phytoplankton are washed out of the river arms during the wet season, but the arms favour blooms during the dry season—possibly because of limited flushing and availability of nutrients (McKinnon et al. 2006). Distribution of Chl *a* is generally uniform with depth in the water column; except that in the wet season, near-surface levels were greater than deeper (2 m vs. 20 m), possibly resulting from light limitation. Tidal mixing is likely to work against phytoplankton, even motile forms, migrating to optimal light levels, and Padovan (1997) has suggested that turbulence keeps phytoplankton in suspension, whilst bed shear stress will resuspend benthic phytoplankton.

Pelagic primary production in the tropics is dominated by picoplankton (cell diam. <2 µm – e.g. cyanobacteria and pico-eukaryotes); Padovan (1997) also tabulates the dominance of the smallest cell sizes in his cell counts from three locations in Darwin Harbour. The prochlorophyte *Synechococcus* is a ubiquitous species; during the wet season, it is displaced to the outer harbour, but is distributed harbour-wide through the dry season (McKinnon et al. 2006). A greater proportion of Chl *a* is in larger cells (>10 µm, e.g. diatoms) during the dry season (39% c.f. 22%) in the arms of the harbour.

A very recent survey of Darwin Harbour's East Arm has shown a more general shift in community structure between the wet and dry seasons (Dostine 2013); phytoplankton are least abundant, but most diverse during the former. Diatoms (with *Chaetoceros*, *Bacteriastrum* and *Asterionellopsis*, typical of tropical marine waters) were just over half of the summed cell density and dinoflagellates were a little under 30% for the survey period June 2010 to June

[3] Tidal exchange quite often underestimates residence times in upper arms of Darwin Harbour; and therefore, can overestimate flushing rates.

2012. Weak correlation was noted for the microalgal community with salinity and nitrate (explaining <40% of the variation), which suggests that other factors are involved (see Section 2.1). Harbour location influenced community structure; communities differed as a function of N concentration.

So far, we have considered only the phytoplankton and phytoplankton dynamics; their community composition will be influenced by nutrient ratios (C:N, N:P and N:Si; Harris 2001b) and availability of micronutrient metals—deficiency or excess (Butler 1998). As we have remarked above, phytoplankton remove nutrients from seawater in the Redfield Ratio proportions (C:N:P 106:16:1), and phytoplankton production (with associated nutrients) is generally thought to be efficiently remineralised and recycled. Therefore, they do not themselves cause gross changes in nutrient ratios (with the possible exception of diazotrophs augmenting N). The dissolved N:P ratio outside Darwin Harbour (Timor Sea) is 30:1, but inside the harbour it is less than Redfield Ratio and down at 4.9:1 for dissolved inorganic N and P (DIN + urea : phosphate; Burford et al. 2008). McKinnon et al. (2006) estimated depletion time for depth integrated DIN stocks of 1.6 d in the wet season and 0.8 d in the dry season; the equivalent estimates for phosphate were 3.3 d and 6.8, respectively. This they indicated was further evidence of N limitation for phytoplankton in Darwin Harbour. Indeed, it is also evidence that bacteria are active, because they have the potential to radically alter nutrient ratios. We have already indicated that denitrifying bacteria are postulated as the main agents for causing the change of N:P ratio in Darwin Harbour, and in estuaries and coastal waters generally, through their removal of DIN as N_2.

There is currently no data available on the heterotrophic bacteria in Darwin Harbour. It is possible that they might exploit situations that phytoplankton struggle under. For example, with freshwater flow in tidal creeks during the wet season, the phytoplankton community declines (Butler et al. 2005), possibly as a result of increased turbidity. Such conditions, along with increased organic carbon (bioavailable) could favour heterotrophic bacteria. If such did eventuate, and more widely in the harbour, then it would be conceivable that heterotrophic bacteria play an important role in nutrient cycling (e.g. denitrification) during the wet season.

We have to this point considered a 'bottom-up' perspective on primary production in Darwin Harbour. Zooplankters, from a two-year study (2004–06) of the water body, are dominated by mesozooplankton (>73 µm), of which 94% of these were copepods (Duggan et al. 2008). Burford et al. (2008) reported dilution experiments that showed microzooplankton grazing rates accounting for up to 85% of primary production. These results suggest that 'top-down' control of phytoplankton biomass is a possibility. Harvesting of phytoplankton by zooplankton releases nutrients during the act of consumption, but copepods are also known for faecal pellets that are effective in transferring nutrients directly to the sediments below (Frangoulis et al. 2004).

Finally, although not pelagic, marine sponges have a profound influence on the water column. They comprise a diverse and significant component of benthic communities aiding in important functional roles—including for sponges, benthic-pelagic coupling associated with their immense filtering capabilities (Bell 2008). Darwin Harbour is no exception, with previous systematic studies highlighting the abundant and diverse sponge populations (e.g. Alvarez et al. 2000, Alvarez & Hooper 2009, 2010). Sponges form intimate associations with microbes (holobionts), and through these partnerships contribute to important functional processes such as nitrification (Schläppy et al. 2010), denitrification (Schläppy et al. 2010, Hoffmann et al. 2009) and anammox (Hoffmann et al. 2009, Mohamed et al. 2010). To date, much of the work on denitrification and anammox in sponges has focused on a species common to the North-East Atlantic and Artic, leaving a gap in the knowledge of the functional potential of sponge

species in Northern Australia. Given the diversity of sponges in Darwin Harbour, it is likely some species are sinks for nitrogen.

2.3. Inputs of nutrients to the harbour

The largest source of nutrients in Darwin Harbour is suggested from the sea (Beagle Gulf); Burford et al. (2008 and references therein) reported net ocean inputs of 15,015 t N/y and 1,087 t P/y. The same researchers also reported substantially lower atmospheric inputs via N fixation by the intertidal mudlflats (2,733 t N/y), subtidal sediments (1,956 t N/y) and mangroves[4] (220 t N/y). N fixation in the water column was not considered to be a major input (Burford et al. 2008), owing to the low concentrations of chlorophyll a in Darwin Harbour (McKinnon et al. 2006). Moreover, N input from direct rainfall is minor (194 t N/y; Burford et al. 2008 and references therein).

Diffuse source loads from catchment runoff during the wet season would also contribute nutrients to the Darwin Harbour (via rivers and creeks); albeit a relatively minor input compared to oceanic and atmospheric sources. Catchment N and P loads into Darwin Harbour for a typical wet season (1.7 m rainfall) were determined to be 722 t and 42 t, respectively (Skinner et al. 2009). Catchment loads entering Darwin Harbour are proportional to the annual rainfall, so nutrient loads can vary from 413–1,150 t N and 22.7–67.1 t P over the range of wet season rainfalls (i.e., 1.0–2.7 m; Skinner et al. 2009). Most of these nutrients are derived from the two largest sub-catchments: Blackmore River (63,471 ha; 191 t N and 8.7 t P during average wet season) and Howard River (54,163 ha; 174 t N and 8.95 t P during average wet season).

Darwin Harbour catchment has an area of 2010 km^2; ~80 % is undeveloped, non-pristine savannah woodland, ~11 % is urban land-use (i.e., residential living, manufacturing/industrial uses, roads and fence facilities) and the remaining land-uses are rural (Skinner et al. 2009). These different land-uses can influence the nutrient loads entering Darwin Harbour. Blackmore River and Howard River catchments are largely undisturbed/rural but they contribute a substantial fraction of catchment nutrient loads to Darwin Harbour because of their sheer size. Although representing a small fraction of the catchment, urban land-use contributed a disproportionately higher nutrient load to Darwin Harbour compared to rural/undeveloped areas (Townsend 1992; Schult 2004; Skinner et al. 2009). Urban development changes overland flow paths, reduces infiltration to groundwater and decreases the time runoff takes to enter rivers and creeks (Skinner et al. 2009); this effectively increases the volume of runoff, and thereby, increases transportation of pollutants into receiving waters and ultimately Darwin Harbour.

Higher concentrations of TN and TP were reported for urban (Moil and Karama) and industrial (Winnellie) catchments compared to rural/undisturbed catchments (Kernohan and Townsend 2000; Padovan 2001a; Padovan 2001b; Padovan 2002; Schult 2004; Skinner et al. 2009). Future developments within the catchment are likely to increase nutrient loads into Darwin Harbour. For an average wet season, proposed future developments could increase annual loads of N and P to 991 t and 70 t, respectively (Skinner et al. 2009); this equates to increases of 37 % TN and 67 % TP.

A large proportion of nutrients entering Darwin Harbour from predominantly rural/undisturbed catchments (e.g. Blackmore, Elizabeth, Howard, West Arm, Woods Inlet) are probably not readily bioavailable, as P largely exists as particulates and most N compounds

[4] Wilson et al. 2004 reported 1.28–3.38 kg N/ha and 0.14–0.96 kg P/ha can be exported into the harbour with mangrove drainage over the tidal cycle.

are likely to be organic (Padovan 2001b, Drewry et al. 2010a, Drewry et al. 2010b, Darwin Harbour Region Report Card 2012); whereas ammonia, nitrite and nitrate are minor constituents of the N pool but have ecological significance. Nutrients from aquaculture operations in the Blackmore River catchment will be bioavailable, but they are estimated as a minor load (~1%; Julia Fortune, personal communication).

In contrast, nutrients from urban (Moil) and industrial (Winnellie) catchments are likely to be more bioavailable due to greater fractions of dissolved P and N compared to rural/undisturbed catchments (Schult 2004; Skinner et al. 2009); the latter predominantly exists as nitrate. The greater proportion of nitrate derived from urban/industrial catchments may be attributed to the sparsity of vegetation (compared to rural/undisturbed areas), which would typically intercept and take up dissolved nitrate (Skinner et al. 2009).

Schult (2004) observed seasonal trends in the concentration and fractionation of nutrients from rural (Bees Creek and Elizabeth River) catchments; elevated TN, TP as well as dissolved N and P were typically detected in the early wet season, but they rapidly decreased within the first two months of the wet season. This first flush of nutrients was also observed in an industrial catchment (Winnellie; Padovan 2001a). In addition to seasonal effects, tidal cycles are known to influence the flux of loads in and out of Darwin Harbour. During neap tide, TN exported to Darwin Harbour from Blackmore river estuary was greater than that imported by up to 56 % (Wilson et al. 2004). However, during spring tide, TN imported into the estuary was greater by 10 %. Wilson et al. (2000) reported that TP load exported to Darwin Harbour was greater than that imported by at least 20 % (Blackmore River estuary, spring tide) and up to 45 % (Middle Creek, spring neap tide).

In addition to catchment loads from diffuse sources, nutrients can also enter Darwin Harbour via point sources; these are mainly from wastewater treatment plants. Based on 2006 discharge data, 321 t N/y and 102 t P/y entered Darwin Harbour from wastewater discharges (Skinner et al. 2009). In comparison to catchment loads, wastewater contributed a significant fraction of the annual load of nutrients (particularly P) into Darwin Harbour (Townsend 1992; Padovan 2001a; Skinner et al. 2009); 71 % P and 31 % N were due to wastewater discharges (Skinner et al. 2009). Point source nutrient loads are likely to increase as the population grows. Skinner et al. (2009) estimated wastewater-derived P and N could increase up to 80 % and 50 % of annual loads, respectively, with a doubling of the population.

Skinner et al. (2009) estimated point and diffuse sources contributed 1,043 t N/y and 144 t P/y into Darwin Harbour, which is relatively minor compared to oceanic (15,015 t N/y and 1,087 t P/y; Burford et al. 2008 and references therein) and atmospheric inputs (4,909 t N/y from N fixation by intertidal mudlflats, subtidal sediments and mangroves; Burford et al. 2008). Hence nutrient loads from point and diffuse sources related to human activity is unlikely to substantially affect biogeochemical processes on a whole of harbour scale, but may be significant at local scales (e.g., tidal creeks or upper reaches of estuary; Skinner et al. 2009).

While nutrient loads from land-based diffuse and point sources have been reported widely, there is a lack of information on groundwater nutrient inputs into Darwin Harbour. Although most rivers/creeks cease to flow by June, the Howard River and Berry Creek continue to flow during the dry season from groundwater inflows (Skinner et al. 2009 and references therein). Hence, groundwater nutrients can potentially contribute to loads to Darwin Harbour, albeit minor compared to oceanic and atmospheric inputs. Some insights come from neighbouring catchments to Darwin Harbour: consistently elevated nitrate concentrations were measured in the Douglas River (near Oolloo Road bridge in Daly catchment; Townsend et al. 2002, Schult and Metcalfe 2006); this was attributed to contaminated groundwater, possibly from agricultural developments in the region, but may also result from weathering of dolomite rock

(Coughanowr 2001) in this catchment (and could also apply to Berry Creek dolomite outcrops in Darwin Harbour catchment). Schult and Metcalfe (2006) estimated the nitrate load of Douglas River was ~17 kg/day, which was 16 times greater than that for the Daly River. All other nutrient loads were greater in the Daly River, in accordance with its much larger flow volume (Schult and Metcalfe 2006). The high nitrate concentration in the Douglas River can potentially adversely influence the Daly River water quality. Despite the elevated nitrate concentration in the Douglas River, high phytoplankton concentrations were not measured downstream owing to phosphorus limitation in freshwaters (Townsend et al. 2002).

2.4. Fates of nutrients

The fate of nutrients depend on their biogeochemical properties, the pathways open to them and the environmental conditions that apply in the subject domain (in this case, Darwin Harbour). Despite a rich supply of information on nutrient inputs and at least reasonable knowledge, albeit with some gaps, of cycling and standing stocks in the harbour itself, there is scant information on fates of nutrients, apart from a report concerning mangrove sediments (Welch et al. 2008), and another concerning short-term fate in tidal creeks (Smith et al. 2012).

Nitrogen and phosphorus differ markedly in the pathways open to them. We have summarised these above (Section 2.1 and Figures 2–4). The ultimate sink for both is burial in estuarine, coastal or even offshore marine sediments. However, it is a case of how long they can keep cycling to avoid that terminal fate (in sub-geological time). Nitrogen has more options here, because it can evade to the atmosphere as N_2, and other volatile inorganic (e.g. N_2O and NO) and organic forms (e.g. short-chain alkylamines). The only volatile form of P is phosphine that is so highly reactive and only produced in such trace quantities under strongly reducing (anoxic) conditions that it can be ignored (Weber 1999).

When considering effective nutrient assimilative capacity for a system, such as Darwin Harbour, the sinks that are relevant are of two types. The first are those that remove the nutrient element from the system entirely; the second—within the system—quarantine or sequester it sufficiently long that natural correction or remedial action has time to act. Denitrification and deep burial in sediments are examples of the former; locking up nutrients in the trunk of a mangrove might be an instance of the latter. However, the assimilation of nutrients by phytoplankton would not satisfy the second criterion if the bulk is returned to the water column by in-situ remineralisation or diffuses back across the sediment-water interface after early sedimentary diagenesis to be available for the next growth period of phytoplankton. Because then, the recycled supply of nutrients combines with inputs from terrestrial run-off, WWTP discharges and diffuse urban supply to increase the available nutrient stock year by year.

The Port Phillip Bay Environmental Study (Harris et al. 1996) revealed the importance of denitrification in the bay's sediments in dealing with N in the nutrient load delivered directly from the urban area of Melbourne, or via the Melbourne Water Western Treatment Plant at Werribee.

The most suitable analogue for discerning the probable fates of N and P (and if required, C) in Darwin Harbour would seem to be the work of Alongi and McKinnon (2005). Along with terrestrially derived sediments, they considered the cycling and fate of nutrients to the coastal zone of the Great Barrier Reef shelf. Although the GBR differs in not being a macrotidal system, their study site at Princess Charlotte Bay is at a latitude very similar to Darwin. Their major findings form a basis for testing in Darwin Harbour:

- microbial communities in coastal waters and in unconsolidated sediments metabolise nutrients equivalent to the entire dissolved and particulate nutrient load arriving from land;
- nearly all nitrogen is ultimately returned to the atmosphere via denitrification;
- there is little net burial of nutrients in subtidal sediments;
- despite significant re-suspension, sedimentation fluxes are sufficient to balance benthic mineralisation rates;
- mangroves and tidal flats trap, transform, and store a disproportionate amount of sediment and organic matter;

3. Nutrient assimilative capacity in Darwin Harbour—thresholds and the means of assessing them and predicting their advent

Underlying the concept of nutrient assimilative capacity is the desire to retain a system—in this case a coastal water body—in its present state or even to return it to an earlier favoured one. As we commented at the outset, it is common that the concept is invoked when a negative change has occurred, for example, deterioration or loss of a valued component of an ecosystem (seagrass, corals, dugongs or others). Then, it is presented in the sense that nutrient assimilative capacity has been exceeded. A better application would be in a preventative framework with a capacity for forewarning. The payoff is not only the retention of the prized species, but the avoiding of a severe penalty for crossing critical thresholds in the form of system hysteresis (Harris 1999), whereby the earlier cost of pre-emptive action is far exceeded by the cost of correction.

Another shortcoming of some impressions of nutrient assimilative capacity is that it applies to the entirety of a water body. This view of averaging over a system, such as Darwin Harbour, has an inherent risk: it ignores the diversity of estuarine environments, temporal changes and other factors causing patchiness. Some locations will be more sensitive to nutrient inputs, because of decreased assimilative capacity arising from poor flushing, low light, differences in planktonic or microbial community at the base of the ecosystem, or other ecological factors. Overloading these sites with nutrients will cause localised degradation. The striking example for Darwin Harbour is Buffalo Creek. It is conceivable that because individual tidal creeks are small components of the harbour that a couple more instances like Buffalo Creek would still not exceed an averaged harbour-wide estimation of acceptable nutrient assimilative capacity. What damage would this cause in possible loss of biodiversity and habitat, as well as cultural and recreational values? The heads of the tidal creeks are small zones spatially, but they represent a finite number of special niches.

Traditional environmental indicators[5], such as phytoplankton biomass (using Chl *a*), seagrass area and species, mangrove area and species, or even concentrations of nitrogen forms (Ward et al. 1998) have their place. However, in most cases they are critical threshold indicators (and most would be listed under 'condition' indicators; N is a pressure or stressor indicator). If they have been crossed or triggered, then it is likely that damage to the ecosystem has been done that is not easy to rectify. Certainly, they have their place in modelling simulations, usually as the 'end-game'—arriving at situations that are not desired.

Limited research has been done in selecting environmental indicators for estuarine and coastal systems that are harbingers of troublesome change in trophic status. These indicators need to be selected—and verified—not only so that they might be used in environmental monitoring, but also that they might be tested in ecohydrological / biogeochemical models to reveal that they do indeed precede, in sequence, the critical threshold or condition indicators. In an extensive study of temperate estuarine lagoons along the NSW coast, Scanes et al. (2007) have remarked on the need to use a range of indicators "to assess trends in ecological condition of an estuarine ecosystem, particularly where stressor levels are not great". They noted for their study lagoons that using water-quality indicators as the sole means of

[5] Some that were selected nationally—e.g. turbidity to infer phytoplankton effect on light (rather than inorganic suspended sediment) —are appropriate for temperate regions of Australia, but entirely unsuited for Darwin Harbour and Top End coastal waters.

assessment was an inadequate practice. We shall look to select a set of indicators as a 'multiple-strands-of-evidence' approach in the next section.

3.1. Indicators of thresholds in nutrient assimilative capacity in a Northern Australian macrotidal estuary

Our discussion here should be more universal than just Darwin Harbour, although it is the focus for our recommended application. The precepts should be applicable to other tropical macrotidal (and likely mesotidal) estuaries draining similar Northern Australian catchments.

The fundamental condition indicator Chl *a* concentration needs to be included in our set, because it is a benchmark for the transition—a state change—from clearer, macrophyte-dominated systems to more murky plankton-dominated ones (Harris 2001b). Chl *a* has been routinely used as the critical output result for different N loadings in estuarine biogeochemical models (e.g. HES 2000). It is also the indicator that will used to calibrate other selected indicators in model studies recommended in later sections here.

Dissolved Oxygen (DO) is another indicator that would be, at first inspection, included in the critical category. However, its declining trend can also be a useful portent of change. It will be of particular benefit in identifying deleterious conditions in vulnerable locations in the harbour as a result of location or temporal factors (tides, springs/neaps or seasonal). For example, in a useful model system, a mesotidal tropical estuary with fringing mangroves adjacent to the Hinchinbrook Channel in Queensland (at Lat. ~18° 20′ S), became quite hypoxic (<2 mg L^{-1}) during wet-season low tides (McKinnon et al. 2010). In this case, the increased N load was imposed by sea-cage finfish farming.

Since it is N that is the primary limiting nutrient in Darwin Harbour and most estuaries (acknowledging that P co-limitation can possibly manifest in brackish waters of the upper reaches and in surface-water outflow during the wet season), it is with the cycling of this nutrient that we might have some of the most suitable threshold indicators. At this point, it is not possible to be definitive about which step in the N cycle will prove to be the most useful and sensitive, not to mention the most pragmatic. We are not aware of published research that might provide guidance to the selection of such an indicator. Nevertheless, it appears that a molecular technique specifically targeting the algae, bacteria and archaea genes involved in N cycling (metagenome or transcriptome) will offer the advantages of specificity and sensitivity, and that it will be 'triggered' before conventional monitoring of water quality would identify a change. We do anticipate that a molecular technique targeted at bacterial activity will be the favoured approach, because of the intimate association of bacteria with all steps of the N cycle and because it can identify the active pathway when the end products are the same, for example denitrification and anammox.

From our discussions above (Section 2), a few options for indicators in the N cycle might be put forward. Denitrification would seem to be a pivotal step in the N cycle as an N sink, and postulated as the cause of the pervasive N limitation of primary production. Therefore, a suitable indicator might monitor the population density or activity of the denitrifiers. Recycled production in the water column is associated with ammonia as the N source; it is turned over quickly under N limitation. If oxidised forms of N (NO_x – nitrate and nitrite) become more readily available, arising from human activities, they fuel 'new' production; as a result ammonia turnover falls away. A molecular means to track ammonia use by heterotrophic bacteria would furnish a useful indicator. We have also commented earlier on the critical balance between nitrogen fixation and denitrification on intertidal mudflats being influenced by labile organic C. If this carbon substrate is an indication of increasing anthropogenic input and also the 'health' of N cycling, then molecular techniques to rapidly evaluate the balance between N

fixers and denitrifiers in these sediments would be insightful. Our intention is not to be prescriptive here; this is an area for ground-breaking applied research.

Finally, the omission of potentially sensitive biological indicators (e.g. seagrass – canopy cover, standing crop [dry wt/shoot density], epiphyte abundance, etc. (Scanes et al. 2007 and references therein); macroalgal biodiversity and abundance) does not reflect on their suitability for monitoring trophic status. Their impediment is that they are likely to be more difficult to model than the rate of steps in the N cycle (mediated by bacteria).

3.2. A modelling approach to nutrient assimilative capacity, and scenario testing

There are good examples nationally of sophisticated ecohydrological or biogeochemical[6] models used to model nutrients in Australian estuaries and coastal waters—especially to study the effects of increased N loadings: e.g. Port Phillip Bay (Harris et al. 1996, Murray & Parslow1999), Brisbane River/Moreton Bay (McEwan et al. 1998), Swan River estuary (Robson & Hamilton 2004) and South-East Tasmania (Wild-Allen et al. 2010). Almost without exception, such models are applied in temperate and subtropical zones.

One ecohydrological model that has been sketched out for Darwin Harbour is that of Wolanski et al. (2006). It is underpinned by the open-access RMA suite of models. RMA2 – a finite-element, depth-averaged hydrodynamic model, and RMA11 – a water quality model (with cohesive-sediment transport) have been used to describe the hydrodynamics and sediment transport in the Darwin Harbour (Williams et al. 2006), and are used in a package for numerous applications associated with the harbour.

A very basic application of the RMA2/RMA11 package has been used to model total N and total P in Darwin Harbour with single decay coefficients each to simulate their uptake by biogeochemical processes (Fortune & Maly 2009). The model was run "to estimate the total maximum pollutant loads [from catchment run-off and WWTP discharge] to achieve water quality objectives". Such an over-simplification of the N and P cycling, and the other biogeochemical influences over them, was doomed to fail to estimate a 'nutrient assimilative capacity' of the harbour for all of the reasons presented in the preceding sections. It was acknowledged in the report that the model needed to be enhanced with information on N and P cycles among other factors.

It seems timely to review the water quality modelling of Darwin Harbour to optimise approaches for effective management of the water body under various development and waste-water treatment scenarios. The ten-step sequence advocated by Robson et al. (2008) for process-based biogeochemical models of estuaries that can be used retrospectively seems a worthwhile approach to reflect on requirements, assess knowledge gaps, and bring this together in a systematic and holistic manner.

We shall not undertake that task here; it is the substance of another project. The outcomes of the review using Robson and co-workers' (2008) approach can be integrated with the improvements that have been identified by David Williams for the RMA11 model:

- Time series of nutrients fluxes at the ocean boundary
- Upstream and diffuse sediment-nutrient dynamics
- Speciation of Total N and Total P constituents so that the bioavailable concentrations are better defined

[6] The two descriptions will be used interchangeably.

- Rates of interaction of nutrients with phytoplankton and zooplankton
- Rates of interaction with nutrients and sediments
- Effect of sediment concentration on light availability affecting both pelagic and benthic productivity
- Microbial interaction with nutrients and sediments
- Effect of salinity on cohesive sediment dynamics and nutrient interactions
- Zonal differences in sediment-nutrient interactions

Very recently, work has been carried out with the RMA11 model for Darwin Harbour to get the WQ modelling suite operative. The model inputs are the forms of N and P, as well as DO and sediment relations; it predicts changes to microalgae and zooplankton populations.

Improvements with data coverage and process understanding for nutrients and other water- and sediment-quality variables need to proceed in parallel with improvements to the model, or even precede them if the model is not well developed for a particular process or set of conditions. Only with better observational and experimental data will the revised and enhanced model be calibrated and effectively validated.

It should be realised that in many cases, that information for water/sediment quality and biogeochemical processes in Australia's tropical coastal seas (especially northern waters) is non-existent or deficient. In some cases, it will require additional monitoring; in others it will require experimental work in microcosms, incubators, flumes and other simulators of the tropical aquatic environment. Examples of the latter are likely to include the rate constants of reactions/steps in the nutrient cycles.

Application of an ecohydrologic model to estimation of nutrient assimilation capacity—scenario testing and more

Once a fully functional ecohydrologic model is in place, validated and implemented, it can be run to identify any remaining data gaps (much in the vein of Wild-Allen et al. 2011, but comparing the optimised sampling program with the existing monitoring sites to identify deficiencies). After which the model can be run in a number of modes:

a) *scenario testing*, where existing conditions and revised nutrient loadings (in line with proposed urban/industrial development, modified WWTP discharge figures linked to plant improvements, etc. – see Section 2.3) are compared with water and sediment quality objectives;

b) *vulnerability resolution*, where existing conditions are used to identify localities that are most at risk of approaching or exceeding the threshold indicators identified in Section 3.1 (for example, conditions verging on hypoxic or even oxygen-deficient during low tides in the wet season (per McKinnon et al. 2010); it is presumed that tidal creeks and estuary arms with longer residence times of stratified bottom waters will be most at risk);

c) a combination of a) and b) for *refined scenario testing*.

As further developments proceed with threshold indicators (e.g. pin-pointing of steps in N cycle, and possibly other nutrient cycles, that are most sensitive to deleterious change), they should be incorporated into modes b) and c) for updating results.

It is worth reiterating that the applications of the model envisaged here are not whole-of-harbour results, but are targeted to produce results on site-to-site, case-by-case basis. The

latter approach is far more likely to guarantee protection of vulnerable, high-value components of the combination of ecosystems that make up Darwin Harbour.

4. Knowledge gaps and their filling

This section is a brief listing of knowledge gaps (and logically going back to data gaps in some instances), with commentary as necessary. It considers these under three headings: monitoring, process understanding and modelling. In reviewing these gaps, we have decided not to be specific about the order in which they are tackled. We suspect many can be tackled in parallel, because there is not interdependence among them, apart from modelling relying on some new knowledge from process studies or the generation of rate constants (decay coefficients) in experimental studies.

4.1. Monitoring

- Ambient estuarine water quality of Darwin Harbour is monitored by the Aquatic Health Unit (AHU; Department of Land Resource Management), with more specific monitoring being undertaken under license conditions set by the Northern Territory Environmental Protection Agency. Monitoring for turbidity and other water quality parameters by the AHU has been standardised to neap conditions in order reduce the influence of tidal conditions on turbidity and facilitate temporal comparisons. This means, however, that the results are biased toward conditions when suspended solids are at a minimum during the lunar tidal cycle (springs/neaps). According to Padovan (2003), this could also bias results for Chl *a*, total P and metals, and warrants definitive assessment. Some supplementary sampling is suggested in the vein of observations by Wilson et al. (2004) in Middle Arm.
- Dissolved organic N (DON) is overwhelmingly the largest fraction of total N. It is suspected that a fraction of this is bioavailable. A method should be implemented to gauge this fraction. It is also relevant to modelling the N cycle.
- Dissolved oxygen (DO) is one of our threshold indicators. It is not presently being reported as part of the ambient estuarine water quality program, because "Water Quality Objectives are currently under revision". This situation needs to be resolved for such an important parameter.
- Bacterial activity (especially heterotrophic bacteria processing of organic matter inputs – Furnas et al. 2011) is likely to outweigh that of all other life forms in Darwin Harbour. Simple tests should be included with the regular monitoring to characterise densities of key functional groups and their level of activity in waters and sediments.
- Nutrient levels in sediment substrates need only be measured infrequently, because they are unlikely to change rapidly (unless some other critical variable such as DO changes); concentrations of nutrients in sediment porewaters are of interest, but in the context of sediment-water exchange (see Section 4.2).
- Contaminants, such as metals/metalloids, persistent organic pollutants (e.g. organohalides, PAHs and tributyltin), endocrine-disruptive compounds and other toxicants need to be monitored on a semi-regular basis, because they can disrupt biological pathways critical for effective nutrient assimilation. Since sediments are an integrator of contaminants in the water column, they would be the preferred monitoring medium.
- More automated monitoring is needed of water column and sediment variables[7], which either come under the environmental health objectives or are important ancillary data. Furthermore, a goal should be to network these around the harbour and catchment (irrespective of provider), such that data is collected and stored under a unified and accredited data management system. Freedom of access to this data

[7] For example, the benefit of ruggedised, automated turbidity loggers for all-year-round monitoring of sediment and nutrient loads into coastal waters has been well demonstrated in Schaffelke et al. (2007)

should be a driver for a comprehensive view of the total system from which all stakeholders benefit.

4.2. Process understanding

- The largest gap in this category would appear to be measurement of denitrification, which is postulated as the reason for N-limitation in Darwin Harbour. Key areas for information are the intertidal and subtidal mudflats, but corroboration of estimates in mangrove sediments would also be worthwhile.
- Benthic nutrient processing within soft sediments (e.g. mudflats) of Darwin Harbour have been reasonably covered, with the exception of the dot point immediately above and possibly also macrophytes. Hard substrates, and particularly the organisms (e.g. sponges, macroalgae and corals) that reside there, have not been incorporated so far into evaluation of nutrient cycling and assimilation. As we have remarked in the body of the report, sponges owing to their filtering capacity, are a serious omission.
- Nutrient exchanges across interfaces (viz. sediment–water, particle–water, air–sea, etc.) need to be characterised better, in both field and laboratory experiments.
- The preceding three points should go a long way to make this next one possible—the harbour is in need of comprehensive N and P budgets (building on Fortune and Maly (2009), and in the fashion of Furnas et al. (2011)). Currently, terrestrial input data is reasonable, as are standing stocks, but sinks are poorly known.
- The underwater light environment in Darwin Harbour is inadequately known, as is the influence of light (or in reality, the attenuation of light by turbidity) on primary production in the water column and the shallow sediments beneath. For the main body of the harbour, all observations reported are of a net autotrophic system (McKinnon et al. 2006, Burford et al. 2008), but this is not true of the limited number of tidal creeks studied (Smith et al. 2012). Is this also true of the estuary arms in the wet season, and how widespread is the phenomenon? Is light implicated?
- Padovan(2003) indicates that the effect of time-dependent events (e.g. tide, springs/neaps and seasons) on water quality is poorly known for tidal creeks; it is not clear whether more recent studies (Burford et al. 2012, Smith et al. 2012) have resolved this situation adequately.
- Use of stable isotopes of N (^{15}N) and C (^{13}C) should be regularised to assist with assignment of sources of N and C, as should possibly other practical techniques that assist in tracking nutrients' inputs.

4.3. Modelling

A set of modelling gaps were listed immediately before this section, so they will not be repeated here. Additional gaps identified in other reports not covered in the previous list are included:

- Focussed measurements (as/not part of AHU monitoring) in the outer harbour to improve the model's boundary conditions.
- Confirm net input of C and N to harbour from marine sources.
- A constantly evolving conceptual diagram of N cycling (and its confrere elements C, S, P and Si) is needed as the common language among scientists and informed managers responsible for monitoring, process understanding and modelling of Darwin Harbour.
- Although not a gap in itself, improvements in monitoring and process understanding need to be implemented in revisions of the model (as should insights from the modelling be factored back into monitoring or studies to improve process understanding).

5. Summary and Conclusions

For a concept that does not appear to have a binding definition when applied to estuarine waters or coastal seawaters, we have defined it in practice for this report with two provisos:

> ***Nutrient assimilative capacity*** *is the scope of the system to incorporate nutrients into living matter and sediments, so preventing build-up of nutrient concentrations in the water column, with two important provisos—that the nutrient assimilation process within the harbour does not lead to 1) loss of estuarine or coastal biodiversity, or 2) degradation of environmental services of the system.*

With this definition in mind, existing information on nutrients and nutrient cycling in Darwin Harbour has been reviewed. At an early stage nitrogen, N, was identified as the limiting nutrient for primary production in the water body. Our study focussed on this element, but we also paid heed to phosphorus, because the two macronutrients in marine and estuarine systems are so closely intertwined, and phosphorus is seen as the "ultimate limiting nutrient" (Tyrrell 1999) in the oceans. Where needed, other influential element cycles (i.e. C and S) were discussed. From general knowledge on the cycling of N and P, the review moved to a description of the distribution of these two macronutrients in Darwin Harbour, and then focussed on nutrient cycling in key compartments of the system: mangroves, intertidal and subtidal mudflats and the harbour's water column. It concluded with an elaboration of nutrient inputs and fates. Key points for Darwin Harbour include that it is generally an undisturbed system as regards trophic status (i.e. low Chl *a* concentrations, DON dominates forms of N); mangroves are the main primary producer (and an important sequester of carbon and nutrients), with phytoplankton second; along with N, light levels and grazing are constraining primary production in the water column; and heterotrophic micro-organisms are suspected to be pivotal in the breakdown of particulate carbon (and nutrients) entering the harbour. Inputs of nutrients from terrestrial run-off and human activity are currently minor, but localised degradation cannot be overlooked (e.g. Buffalo Creek). Nutrient sinks need to be characterised more fully.

The third section represented an important kernel of our study, because in light of the review, we nominated a set of threshold indicators on the path of changing trophic status for Darwin Harbour. These are chlorophyll *a*, dissolved oxygen and—yet to be identified by research—one or more N cycle indicators (using molecular biology of relevant bacteria). A framework is identified for incorporating these threshold indicators into the relevant RMA model suite and arriving at outputs that should prove beneficial to decision making for an ecologically sustainable future for Darwin Harbour, in the face of increased nutrient loads.

The final section looks at knowledge gaps in monitoring, process understanding and modelling, and how they might be fulfilled with the goal of smoothing the path to robust estimates of nutrient assimilative capacity for Darwin Harbour (see Plate A1 in the Appendix for the state of knowledge for nitrogen in Darwin Harbour). Some important gaps included information on denitrification harbour-wide, the capacity of sponges as nutrient assimilators, and a requirement for more (and automated) monitoring of nutrients and other ecological variables across the spectrum of harbour conditions (tidal, spring/neaps, seasonal and interannual). The estimation of nutrient assimilative capacity of Darwin Harbour can be realised through a combination of observations, experimentation and modelling; a framework has been outlined. Yet, it is *not* a calculation that should be made on a whole-of-harbour basis, but from location to location within the waterway to protect the integrity of ecological components of the full system.

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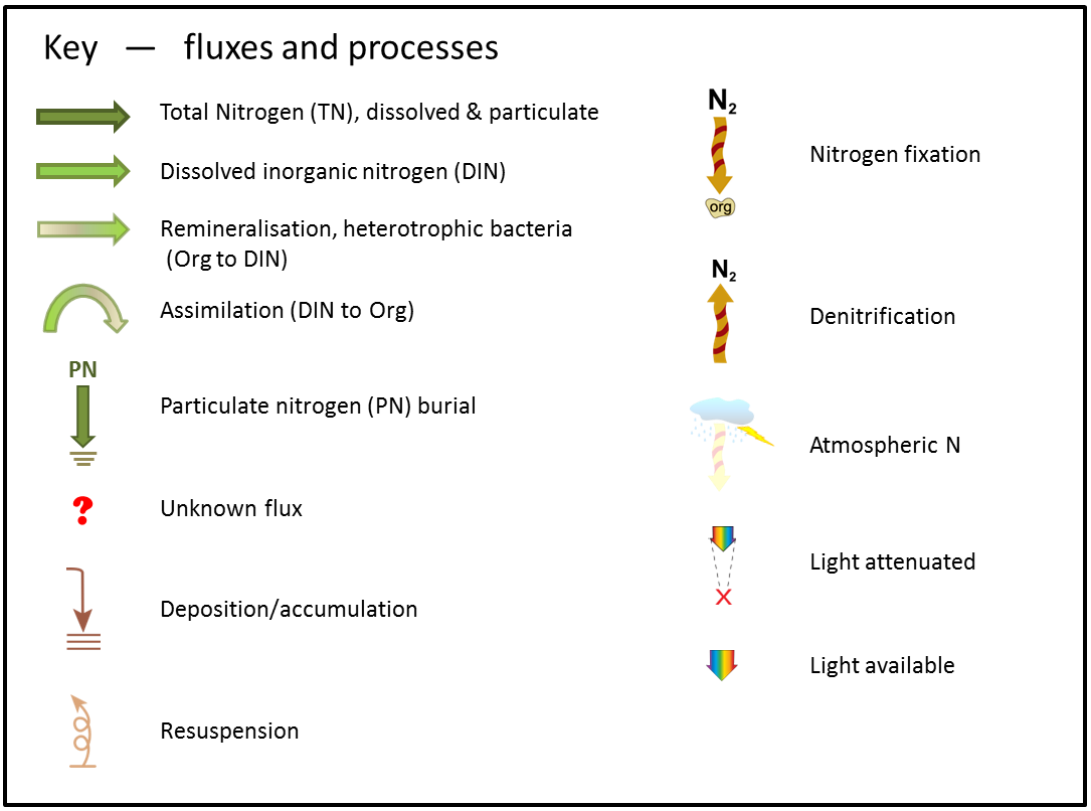
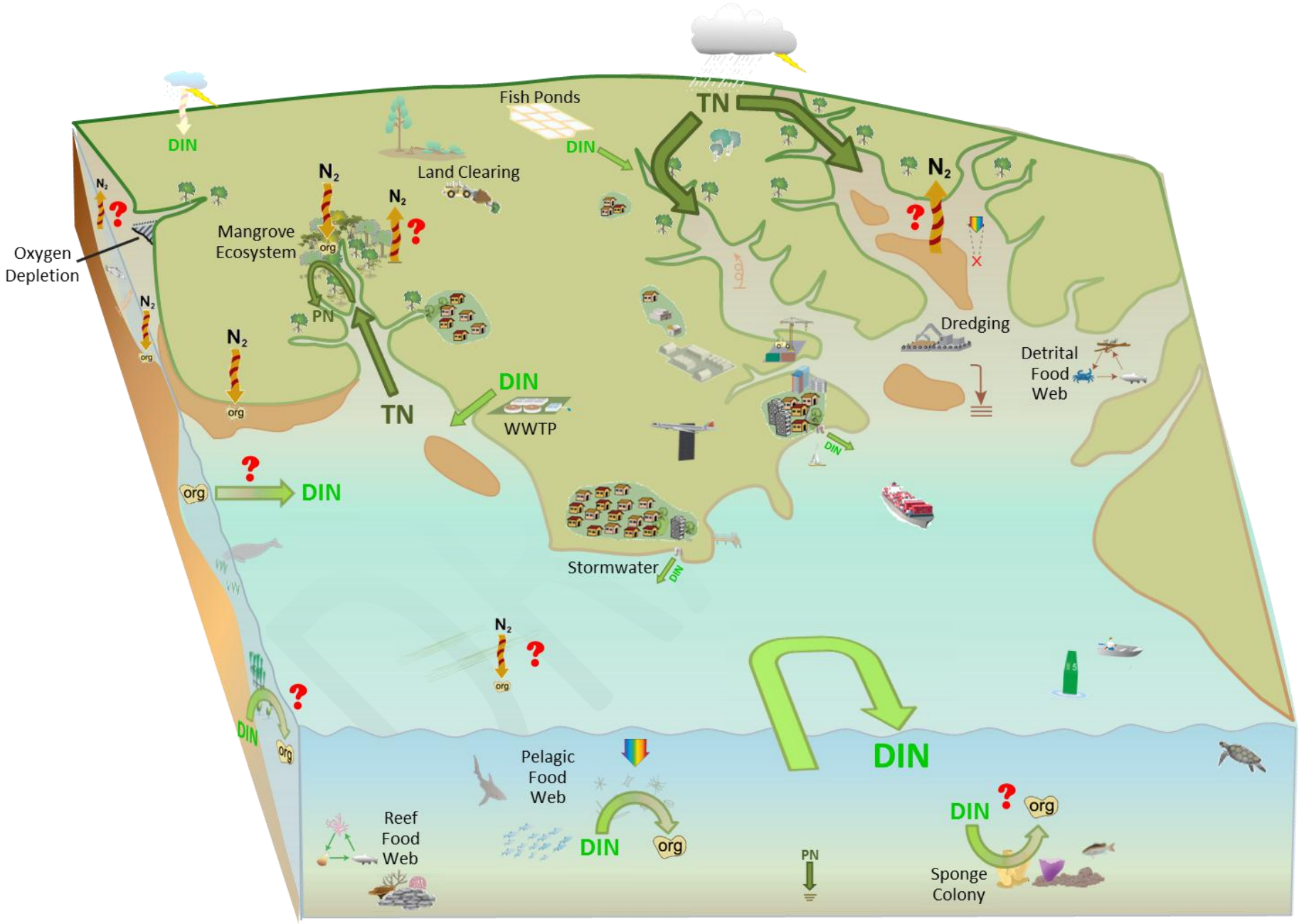
Appendices

Appendix 1:

Plate A1. Depiction of nutrient inputs, cycling and sinks in a stylised Darwin Harbour, including indication of fluxes that are not known. It is not intended to be geographically accurate.

Notes: (a) The size of arrows is broadly indicative of the magnitude of the transfer or flux, except where the question mark indicates that it has not been quantified. (b) Total nitrogen supply via the rivers is very episodic, depending on the rainfall events in each wet season. (c) U-turn arrows (e.g. seawater input of DIN and mangrove processing of TN) are indicative of tidal exchange. (d) Heterotrophic bacteria can process organic matter either to release dissolved inorganic nitrogen (DIN, especially ammonia via ammonification) or transfer nitrogen to the atmosphere via denitrification as N_2 – neither process is quantified. (e) Nitrogen fixation has been directly determined for intertidal mudflats and subtidal sediments and estimated for mangroves (Burford et al. 2008), but is unknown, assumed small, for the water column, although the possible seasonal appearance of *Trichodesmium* blooms has not been accounted. (f) the net effect of mangroves with incoming TN and small amounts of outgoing PN is removal of DIN and DON and some of the PN. (g) Benthic microalgae (as distinct from pelagic microalgae – i.e. phytoplankton) have not been depicted, but may also have considerable nutrient uptake potential on intertidal mudflats or over shallow subtidal sediments. (h) the capacity of other benthic life forms (e.g. sponges and seagrass) to take up nutrients remains undetermined in Darwin Harbour.




DIN
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Depletion
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Sponge
Colony