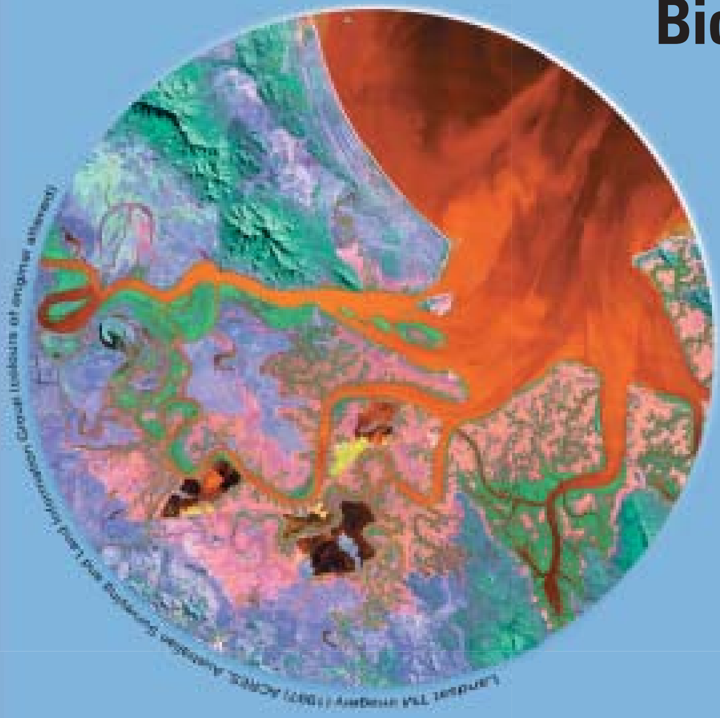
Cooperative Research Centre for Coastal Zone, Estuary & Waterway Management

Technical Report 40



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Biogeochemical modelling and nitrogen budgets for the Fitzroy Estuary and Keppel Bay

B. J. Robson
I. T. Webster
U. Rosebrook

June 2006

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Biogeochemical modelling and nitrogen budgets for the Fitzroy Estuary and Keppel Bay

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Barbara Robson conducted the system scale modelling and analysis, Uwe Rosebrock provided programming and model support, and Ian Webster was primarily responsible for study design and provided critical comment. This report was compiled by Barbara Robson with input from Ian Webster.

Table of contents

List of figures

List of tables

Executive summary

This report describes the implementation of a biogeochemical model of the Fitzroy Estuary and Keppel Bay and the results of the model when applied to three scenarios: a high flow year, a median flow year and a low flow year. The model simulates transport and transformations of nitrogen, phosphorus and organic material in the estuary, as well as primary production by phytoplankton and microphytobenthos (benthic microalgae). The biogeochemical model is embedded in the hydrodynamic model described in Report 38 (Herzfeld *et al.*, 2006) and the sediment model described in Report 39 (Margvelashvili *et al.*, 2006), and has been calibrated to match as closely as possible the observed biogeochemistry of the system, as described in Report 34 (Radke *et al.*, 2006). The application of the model to scenarios that consider changes in flows and sediment and nutrient loads is described in Report 41 (Robson *et al.*, 2006).

The model simulates observed dry-season conditions (August 2004) well and wet-season (February 2005) conditions satisfactorily, although it underpredicts total nitrogen and phosphorus concentrations immediately after a flow event.

The scenario simulations provided quantitative estimates of nitrogen delivery to the ocean under varying river flow regimes and sediment loads. As is the case for sediment delivery (Margvelashvili *et al.* 2006) high floods are likely to play a major role in nutrient delivery to the ocean, and reducing nutrient loads to the estuary during high flow events may have substantial impact on the sediment delivery from the Fitzroy catchments to the Great Barrier Reef lagoon. The impact of variations in nutrient loads from the catchment during low flow years may be less substantial in the short- to medium-term, but may have a greater impact in the long-term due to changes in sediment nutrient stores in Keppel Bay.

Key conclusions from the model results are as follows:

- The majority of particulate nitrogen and phosphorus in the system is very refractory (i.e. it is not readily biologically available), with a mineralisation (breakdown) half-life on the order of 40 years.
- The system is net heterotrophic ñ that is, production relies more on organic material brought in from the catchment than on local primary production.
- Primary production in the water column is tightly controlled by limited light availability in the estuary and inner Keppel Bay and low nutrient concentrations in outer Keppel Bay, and is also subject to top-down predation control by invertebrate grazers.

- The quantity of nitrogen and phosphorus exported to the Great Barrier Reef lagoon responds in a nonlinear way to inflows and loads. Over the long term, nutrients are accumulated in the sediments. The model suggests that there may in many years be a net import of nitrogen from marine sources, although there is a net export during high flow years. This result is surprising and may change if further data become available.

Introduction

Major goals of the Fitzroy Agricultural Contaminants project have been to improve understanding of the function of tropical estuaries and their role in coastal nutrient cycles and to develop understanding and products that can aid management of the Fitzroy Estuary and its catchment. Further, the Fitzroy River has the second-largest seaward draining catchment in Australia after the MurrayñDarling Basin. The Fitzroy River delivers the second-largest amount of nutrients and sediments to the lagoon of the Great Barrier Reef (GBR) after the Burdekin River (Furnas, 2003). The increased delivery of nutrients and fine sediments to the GBR resulting from agricultural activities in the catchments of the GBR since European settlement is thought to be potentially detrimental to the ecological health of the GBR, particularly in inshore regions.

To address this issue, the Reef Water Quality Protection Plan, a Queensland GovernmentñCommonwealth initiative, has recently been implemented with the aim of reducing catchment-derived loads of nutrients and sediments to the Great Barrier Reef lagoon. Predictive modelling and assessment tools, including the biogeochemical model and nutrient budgets described in this report, are among the key outputs of the project. These will be used to estimate how changed loads that may result from the implementation of the Reef Plan will impact on the biogeochemical function of the Fitzroy Estuary and will alter the delivery of nutrients to the GBR lagoon. These products draw together much of the conceptual understanding and quantitative data provided by other components of the study.

Among the primary research questions for the project were:

- Quantitatively, how are nutrients and sediments transported through the Fitzroy system to the Great Barrier Reef?
- Which processes are likely to be important for the dynamics of tropical macrotidal estuaries such as the Fitzroy and what are the roles of biogeochemical processes in intertidal areas?

and

- What is the role of the system as a region for accumulating, transforming and redirecting contaminants from the catchment?

The biogeochemical model, coupled with the hydrodynamic model and sediment model described in separate reports (Herzfeld *et al.*, 2006 and Margvelashvili *et al.*, 2006, Reports 38 and 39, respectively) provides a tool that can be used to explore these questions. Materials budgets, providing estimates of how much nitrogen, phosphorus and sediment material enter the Fitzroy Estuary, how much is removed in the estuary and Keppel Bay, and how much is exported to the Great Barrier Reef lagoon, provide quantitative answers to the second and third questions. This project builds on previous Coastal CRCñsponsored work (Webster *et al.*, 2003; Webster *et al.*, 2005; Margvelashvili *et al.*, 2003) that focused on biogeochemistry and the response of primary production of the main stem of the Fitzroy Estuary. The study reported here further develops the biogeochemical model and expands the geographical extent of the study area to include the major tidal creeks and Keppel Bay to consider interactions with the Great Barrier Reef lagoon.

Besides modelling, there were a series of components of the Fitzroy Agricultural Contaminants project which investigated elements of the systems dynamics. Two of these directly relevant to the biogeochemical modelling activity were the biogeochemical investigations of Keppel Bay and of the intertidal areas in the Fitzroy Estuary. These activities were primarily measurement-based and provided data to support the modelling activities. Their results are reported by Radke *et al.* 2006 and Revill *et al.* 2006 (Reports 34 and 35). A parallel modelling activity examines nutrient transformations and primary production on the extensive intertidal areas of the Fitzroy EstuaryñKeppel Bay system. Its results are presented in Report 47 by Brooke *et al. (*2006*).*

The dominant feature of the freshwater discharge from the Fitzroy River into the estuary is its high degree of seasonal and inter-annual variability. Flows tend to be highest in January through to March, but this is not universally the case. Most of the typical year, the flows in the Fitzroy are fairly modest and for a major proportion of the time they are small and sometimes measured to be zero. During times of zero or low discharge during the winter months, much if not most of the fresh water entering the upper end of the estuary is discharge from the Rockhampton sewage treatment plants.

The extent of the inter-annual variability in annual river flow is illustrated by comparing discharges in 1969 and 1991. The year 1991 had an average discharge of 730 m^3s^{-1} whereas 1969 had an average discharge of only 4 m^3s^{-1}, more than two orders of magnitude smaller. The high average flows in 1991 were mostly due to a flood event with discharges of up to 15 000 m^3s^{-1} which lasted about two weeks and was due to the passage of Tropical Cyclone Joy. A second major flood occurred a month after this.

We anticipate that the response of the Fitzroy EstuaryñKeppel Bay system to freshwater inflows and the loads of nutrients and sediments carried with them will be quite different between wet and dry years. Consequently, we model the system response to three flow scenarios, namely, low flow, medium flow and high flow. Such an approach also provides insight into the physical and biogeochemical functions of the system.

The report is organised as follows. We commence with a description of the model followed by its calibration. The model is compared to observations from a dry-season field campaign and from a wet-season campaign. Next we describe the application of the model to the low, medium, and high flow years. Nutrient budgets are developed from measurements and simulation and compared. Finally, various aspects of the project findings are discussed in the concluding section of the report.

Biogeochemical model setup and application

Model description

This study employs the CSIRO Environmental Modelling Suite (EMS), which includes a state-of-the-art biogeochemical model, directly coupled with a three-dimensional hydrodynamic model, SHOC, (Herzfeld *et al.*, 2006) and multilayer sediment transport model (Margvelashvili *et al.*, 2006) described in detail in separate reports.

The biogeochemical component of the model is similar to that applied to the Fitzroy Estuary previously (Margvelashvili *et al.*, 2003, see Figure 1), but has been extended both geographically and in terms of the nutrients considered. The model simulates the transport and transformation of nitrogen, phosphorus and carbon introduced into the system as well as primary production in the water column and epibenthos. Much of the conceptual development of this model was carried out during the Port Phillip Bay study (Harris *et al*., 1996; Murray & Parslow, 1997, 1999a,b). However, as applied here, the model includes some adaptations for the Fitzroy Estuary and Keppel Bay. For details of model equations and processes, refer to Murray and Parslow (1997). Equations are given in this report only for the *Trichodesmium* submodel, which represents an extension to the Murray and Parslow model.

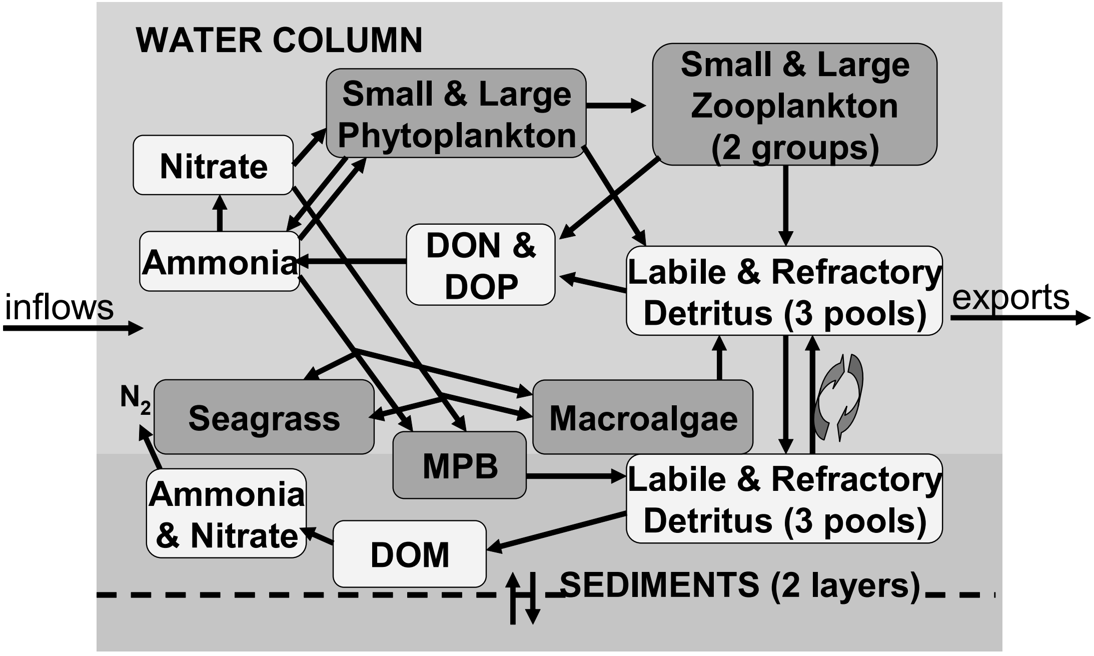

Figure 1. Major nitrogen pathways in the biogeochemical model

For the mudflat-scale model, seagrass, macroalgae and one of the three detrital nitrogen pools are omitted.

Broadly, the model represents a set of pelagic interactions and a set of benthic interactions controlled by analogous sets of functional groups. As illustrated in Figure 1, the model may be conceptualised as a series of stores (boxes) and flows (arrows) of nitrogen, phosphorus or carbon. Some of these flows represent biogeochemical transformations including uptake of nutrients by primary producers, consumption of phytoplankton by zooplankton and organic matter degradation. Coupling the model to SHOC ensures that physical exchanges ñ washout to the ocean, burial of organic matter, settling of detritus to the seabed, and diffusion of solutes between water column and sediments ñ are also represented.

Nitrogen stores in the model include large phytoplankton (diatoms), small phytoplankton (small flagellates), large and small zooplankton groups, microphytobenthos (MPB), macroalgae, nitrogen and carbon in various organic and inorganic forms, and oxygen dynamics. Growth and nutrient uptake by phytoplankton and MPB are represented by a mechanistic model developed by Baird and Emsley (1999). The model employs well-understood relationships for key ecosystem processes and incorporates established literature values for parameters such as maximum growth rates, grazing efficiencies and sinking rates (Murray & Parslow, 1997).

A key feature of the model is its representation of nutrient cycling processes in the sediments. Processes such as benthic organic matter degradation and the return of nutrients to the water column from sediments are particularly important in shallow, energetic systems such as the Fitzroy Estuary and Keppel Bay. Our model adopts the representation of sediment processes used by Murray and Parslow (1997), altered to include three distinct sediment layers ñ a shallow, active surface layer and two deeper sediment stores. This representation is effectively the Type 3 representation described by Soeteart *et al.* (2000), in that it is sufficiently complex that it describes the major processes occurring within sediments in a semi-empirical way, but it is not a fully depth-resolved diagenesis model.

The submodel for microphytobenthos growth in the sediments has also been extended to allow for nitrogen fixation by cyanobacteria when nitrogen would otherwise be the growth-limiting resource. In addition, a model of *Trichodesmium* has been implemented in the model.

Trichodesmium submodel

The cyanobacterium (blue-green algae) *Trichodesmium* is believed to be an important component of pelagic production in Keppel Bay, and *Trichodesmium* blooms washed in from coastal waters were observed during the field campaigns. Also, the transport of *Trichodesmium* by currents is a potentially important vector for the transport of nutrients incorporated within its cell biomass. Hence, it was desirable to enhance the model to improve representation of *Trichodesmium* dynamics.

Trichodesmium is much like other small phytoplankton in most respects. *Trichodesmium* grow by taking up nitrogen and phosphorus from the water column and are grazed by small zooplankton such as copepods (O'Neil *et al.*, 1997). Like *Nodularia*, *Trichodesmium* is capable of fixing atmospheric nitrogen to supplement the available dissolved inorganic nitrogen, giving *Trichodesmium* a competitive advantage when the N:P ratio is low. It has been reported (e.g. Mulholland & Capone, 2000) that *Trichodesmium* is capable of excreting as much as 30ñ50% of fixed nitrogen as dissolved organic nitrogen and so potentially plays an additional role in nitrogen cycling.

In the model, nitrogen fixation is assumed equal to zero if *Trichodesmium* growth is not nitrogen-limited (i.e. if growth is limited by light or phosphorus). If *Trichodesmium* growth would otherwise be nitrogen-limited, sufficient nitrogen is fixed from N_2 to allow growth at the maximum rate permitted by other resources plus a proportional release of nitrogen in the form of dissolved organic nitrogen.

$$Nfix = growth - \frac{growth_{N\lim}}{(1 - FDON)} \qquad \text{(Eqn 1)}$$

where *Nfix* is the rate of nitrogen fixation, *growth* is the growth rate of *Trichodesmium*, $growth_{N\lim}$ is the nitrogen-limited growth rate of *Trichodesmium* and *FDON* is the proportion of fixed nitrogen that is released as dissolved organic nitrogen.

Trichodesmium also differs from most other phytoplankton in that it is capable of taking up dissolved organic phosphorus as well as inorganic phosphorus from the water around it. Hence, phosphorus-limited growth is defined not as a function of the concentration of inorganic phosphorus [DIP], but that of total dissolved phosphorus [DIP]+[DOP].

A final difference is that *Trichodesmium* tends to form colonies that float at the surface. *Trichodesmium* growth is also very sensitive to temperature. Because *Trichodesmium* has a competitive advantage when floating at the surface and wind stress can mix cells down from the surface (and because the layers used in the model are not sufficiently thin to completely represent this), the maximum growth rate of *Trichodesmium* is a function of wind stress and temperature, following the model presented by (Fennel *et al.*, 2001).

Model domain

The system-scale model incorporated the Fitzroy Estuary from the barrage at Rockhampton, Keppel Bay to just south of Keppel Sands, and a number of tidal creeks (Casuarina Creek, Connor Creek, Deception Creek and The Narrows to the mid-point towards Keppel Bay) as illustrated in Figure 2.

A three-dimensional curvilinear grid represented Keppel Bay with 17 vertical layers plus three sediment layers, with horizontal cell widths varying from about 1 km in outer Keppel Bay to less than 500 m in the inner bay. This grid and the hydrodynamic model setup are described in more detail by Herzfeld *et al.,* 2006). The model on this scale has a run-time ratio of approximately 78:1 (i.e. a simulation of a 78-day period takes 24 hours of computer time) when run on a high-performance computer using 12 processors in parallel. This allowed simulations to be conducted that covered the full seasonal cycle over a year.

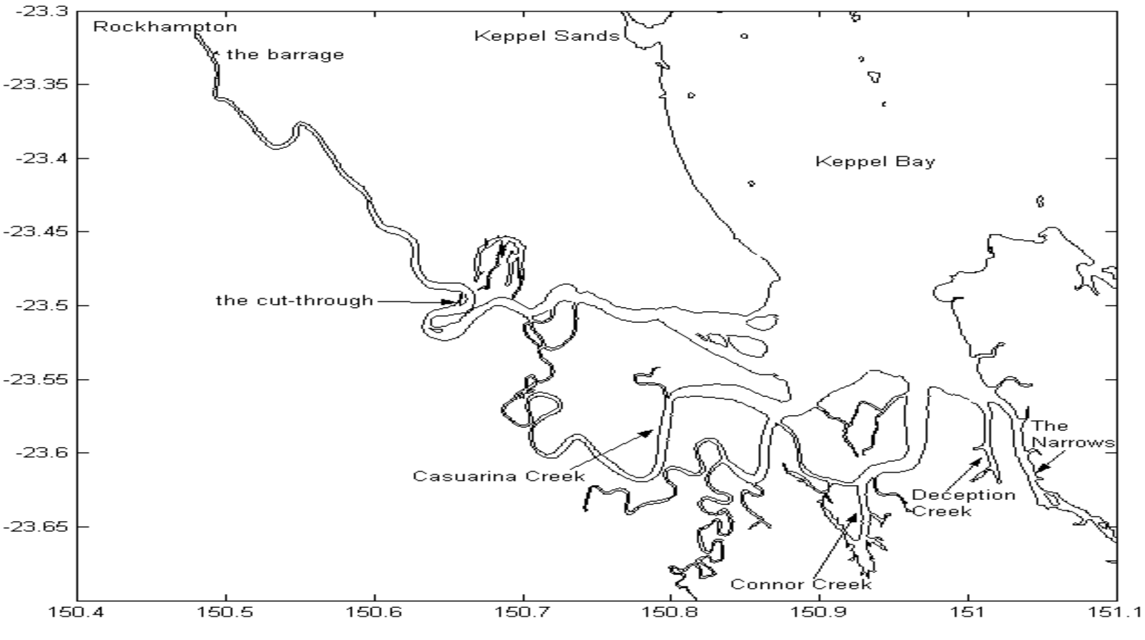

Figure 2. Map of the study domain for system-scale modelling

Model setup

Initialisation

Data collection

Data used for setting boundary conditions and for model calibration and validation were collected as part of another activity in the Fitzroy Agricultural Contaminants project, namely, the biogeochemical investigation of Keppel Bay. This activity collected data on the physical and chemical properties of the water column and sediments during three cruises to Keppel Bay in September 2003, August 2004 and February 2005. Data were also collected on phytoplankton concentrations. The measurements obtained from the first two cruises represent dry season conditions in Keppel Bay. They were undertaken ~5 months after flows in the Fitzroy reduced, whereas the February 2005 cruise was undertaken just after the third of three flow events in that summer and so represents the wet season. The scope and results from this activity are reported by Radke *et al.,* (2005).

Water column

Initial conditions for salt, temperature and suspended solids were set as in the hydrodynamic and sediment dynamic models described above. Concentrations of other dissolved and particulate substances in the water column were initialised with spatially uniform values corresponding to observed concentrations in Keppel Bay during the September 2003 field campaign.

Dissolved oxygen, ammonium (NH_4), nitrate (NO_3), dissolved organic carbon, nitrogen and phosphorus (DOC, DON and DOP), and phosphate (PO_4 ñ in the model, DIP) were determined directly from field observations. The refractory detrital carbon (DetR_C) concentration was set to match the observed particulate organic carbon (POC) concentration. Observed chlorophyll *a* was assumed to be divided equally between large and small phytoplankton. Particulate nitrogen (calculated from the difference between observed total nitrogen and dissolved nitrogen concentrations) was assumed to be mostly comprised of refractory detritus (DetR_N), as this allowed a better model calibration than the alternative assumption that a substantial proportion of this particulate material was more labile. This assumption is not incompatible with the results of bottle incubation studies of sediment material from Keppel Bay (Radke *et al.*, 2005). Of the particulate phosphorus, a proportion was assumed to be refractory detrital phosphorus (DetR_P), and the rest, inorganic phosphorus adsorbed to sediment surfaces. The detrital component was estimated by assuming a molecular ratio of 16:1 between detrital nitrogen and detrital phosphorus.

Benthic sediments

The sediment model was implemented with three sediment layers comprising a surface layer of easily resuspended material 5 mm thick, a mid layer of intermediate characteristics 1 cm thick, and a bottom layer of more consolidated material, 30 cm thick.

Sediment carbon, nitrogen and phosphorus concentrations (mg/g), sediment porosity and wet and dry bulk density were measured at 118 stations in Keppel Bay and the coastal creeks as part of the September 2003 field campaign. From these data, concentrations in mg/m^3 were estimated for each station and interpolated to provide spatially varying initial conditions for the sediments. It was assumed that the majority of benthic sediment nutrients and organic material was in the form of refractory detritus, because this assumption was consistent with the results of sediment incubation studies and allowed a better calibration of the model.

The initial sediment nitrogen concentrations are shown in Figure 3. Note that no observational data are available near Deception Creek or Connor Creek, and so sediment nutrient concentrations for these areas have been set to the spatial mean across the whole domain. The initial distribution of sediment phosphorus and carbon is similar.

Concentrations of dissolved nutrients in sediment pore water were set to spatially constant values adjusted to be in equilibrium with initial water column concentrations.

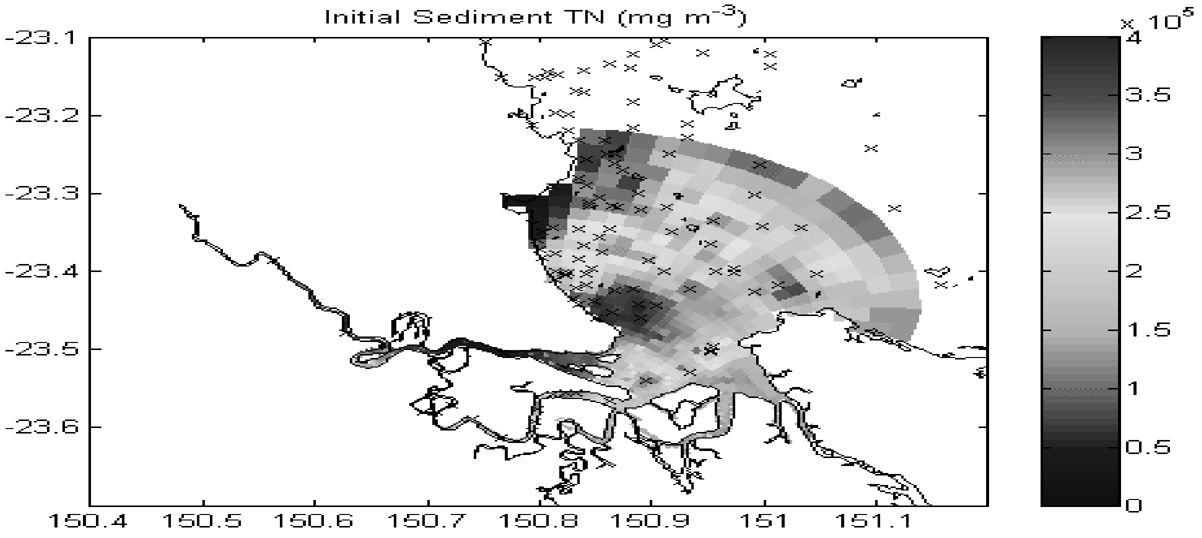

Figure 3. Initial sediment total nitrogen concentrations, calculated from field observations of sediment properties in September 2003. Locations of sediment samples are indicated with crosses

Inflow boundary

Inflow volumes (m^3d^{-1}) and sediment loads were set as in the sediment dynamics model. For the medium flow/calibration year (September 2003 ñ February 2005), actual flows in the Fitzroy River were used for the discharge to the head of the estuary at Rockhampton. For the low flow year simulation, flows from 1992ñ1993 (the second-driest year of the past 15 years, with only a single, small, flow event) were applied, with other boundary conditions as for the calibration year.

For the high flow year, flows were taken from 1998, the wettest year since the 1991 flood. Although the main flow event in 1998 occurred in September and flows continued for six months, this is unusual ñ flow events more typically begin in January or February and continue for up to four months. To arrive at a more typical high flow scenario, therefore, flows for this simulation were derived by taking measured flows for two months from the start of the main 1998 flow event and shifting them in time so that the event started on 1 January, with no inflow after 1 April. The flows used are shown in Figure 4. The total flow for the low flow year was 408 Gl, for the median flow year, 1378 Gl, and for the high flow year, 4433 Gl.

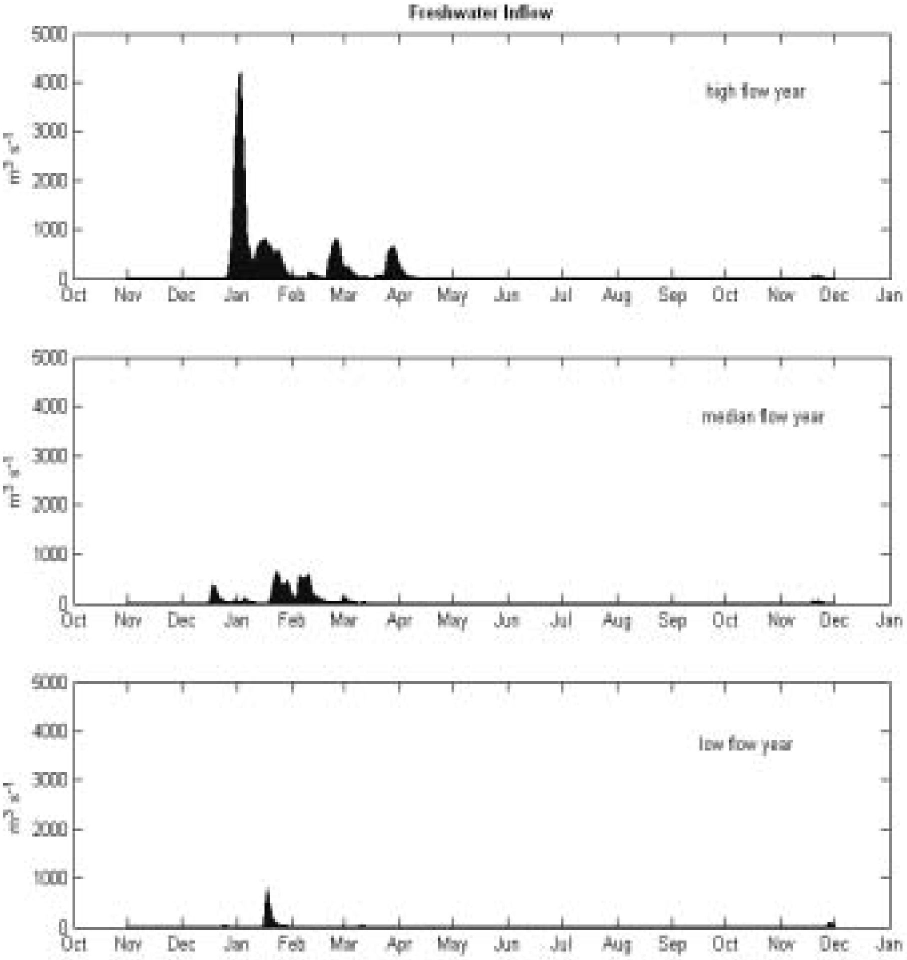

Figure 4. Freshwater inflow for each flow scenario

For all scenarios, nutrient loads to the Fitzroy Estuary from the meatworks and sewage treatment plant near Rockhampton were set to match loads estimated from nutrient budgets for the estuary, as described in the final report for the Phase 1 study.

Analysis of monthly observations of nutrient concentrations just downstream of the barrage at Rockhampton made by the Queensland EPA from 1993 until 1998 indicated that dissolved nitrogen and phosphorus concentrations did not vary significantly with river flow but that particulate nitrogen and phosphorus were correlated with flow. Hence, concentrations of dissolved reactive phosphorus (DIP in the model), ammonia (NH_3), nitrate (NO_3) and dissolved organic nitrogen and phosphorus (DON and DOP) in water flowing into the estuary across the barrage were set to constant values in the model.

The concentration of refractory detrital nitrogen (DetR_N, in mg N m^{-3}) at the inflow boundary was allowed to vary in time, according to the relationship:

$$\text{DetR\_N} = 0.87 \times \text{RiverFlow} + 481$$

This relationship is a linear fit to the EPA data ($R^2 = 0.72$ from 76 data points). Similarly, the concentration of refractory detrital phosphorus (DetR_P, in mg P m^{-3}) at the inflow boundary was determined from:

$$\text{DetR\_P} = 0.28 \times \text{RiverFlow} + 93$$

where RiverFlow is the flow ($m^3\ s^{-1}$) measured at the Gap, upstream of the barrage.

The EPA data do not include measured carbon concentrations, so the refractory detrital carbon concentration (DetR_C) in inflowing fresh water was set to ten times DetR_N. Primary production and other biogeochemical processes of interest are not carbon-limited in the model, so the results are not sensitive to variations in this assumption.

All other inflow nutrient concentrations (e.g. DOC, phytoplankton concentrations and labile detritus concentrations) were set to constant values.

Point sources of nutrients

(Webster *et al.*, 2005) found that the three wastewater treatment plants and two meatworks licensed to discharge into the Fitzroy Estuary provide a small but continuous source of dissolved nitrogen, which was significant in comparison to the negligible flow over the barrage during the dry season. This was implemented in the model as a point source at approximately 150.5°E, 23.4°S (a point in the estuary approximately 18 km above the loop).

Seaward boundary

Concentrations of nutrients and chlorophyll *a* at the seaward boundary were set to constant (low) concentrations that matched observed concentrations in Keppel Bay beyond the seaward boundary in September 2003 and August 2004. This assumption that nutrient concentrations at the outer boundary were constant was unavoidable given the lack of detailed time-series data, but appears to be a reasonable first-order approximation for most nutrient species, at least during the dry season. Nutrient concentrations observed during both dry-season field campaigns (September 2003 and August 2004) in outer Keppel Bay were an order of magnitude lower than concentrations near the mouth of the estuary.

During the August 2004 campaign, hourly water samples were taken at station A, a site corresponding to the outer boundary of the model, over a continuous 12-hour period and subsequently analysed for nitrogen and phosphorus content. Figures 5 and 6 compare the constant boundary condition applied in the model with observed DON and TN over this period. In the case of TN, the actual temporal variation is significant (nitrogen concentration varies by an order of magnitude); however, this variation may be weaker further from the coast.

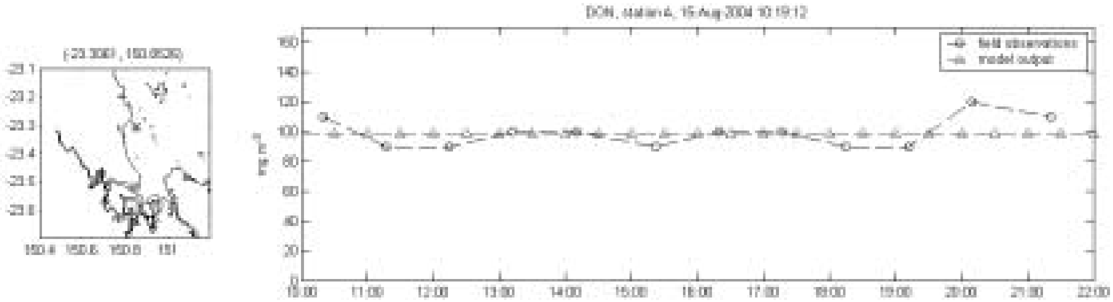

Figure 5. Dissolved organic nitrogen (DON) over 12 hours during the August 2004 field campaign

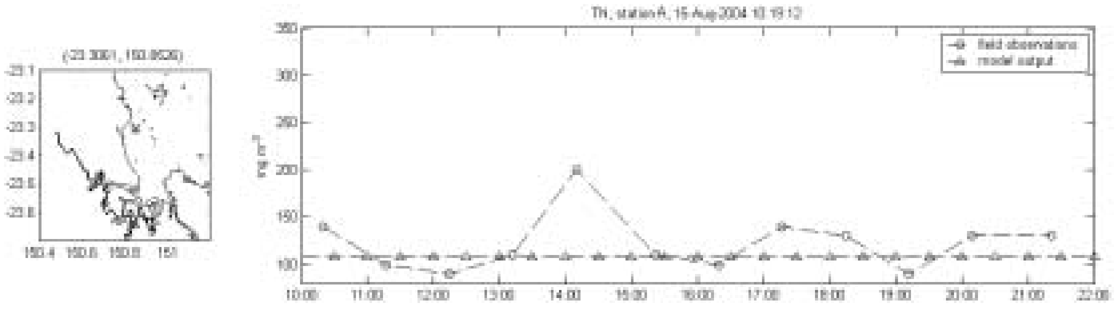

Figure 6. Total nitrogen (TN) over 12 hours during the August 2004 field campaign

Light

Estimated daily solar radiation was obtained from the Queensland Department of Natural Resources, Mines and Water Data Drill, which interpolates meteorological data from the Bureau of Meteorology onto defined geographical points. Data Drill estimates were made at 23.45°S, 150.90°E, a point in Keppel Bay, and applied uniformly to the entire domain. This approach was found to give a better calibration than using a calculated theoretical clear-sky irradiance modified for observed cloud cover, an approach which somewhat overestimates solar radiation.

Timing of simulation

The simulation ran from September 2003 (the time of the first dry-season field campaign) until the end of February 2005 (the time of the dry-season field campaign). This allowed the use of September 2003 field observations for initialisation, leaving August 2004 and February 2005 observations for a comparison of model output with observational data. This period does not coincide with the period of the best calibration of the hydrodynamic model (March 2004 to February 2005, Herzfeld *et al*., 2006); however, it has the advantage of allowing the best use of all available biogeochemical data.

Calibration

The biogeochemical model was calibrated through an iterative approach of adjusting parameter values within defined literature ranges and comparing the resulting seasonal-scale responses with observational data from the three field campaigns (September 2003, August 2004 and February 2005) and other available data (AIMS/GBRMPA chlorophyll measurements at two sites within the domain, nutrient observations within the Fitzroy Estuary during the Phase 1 project (Douglas *et al.*, 2005) and optical estimates of distribution of large and small phytoplankton in Keppel Bay).

Parameter values defining the proportion of inorganic phosphorus adsorbed onto sediment surfaces were calculated from the observed concentrations of suspended sediments and dissolved oxygen, observed dissolved inorganic nitrogen concentrations and particulate inorganic nitrogen concentrations estimated as described for the model initialisation.

Fine-tuning of other parameter values was performed by calibration of the model. Ranges for calibration of parameter values were taken from Murray and Parslow (1997). The aim of calibration was to find values within these ranges that gave model results matching as closely as possible the observed spatial and temporal patterns of total nitrogen, total phosphorus, chlorophyll *a*, dissolved inorganic nitrogen and phosphorus and dissolved organic nitrogen and phosphorus, as well as the spatial distribution of large and small phytoplankton. Approximately 80 calibration runs of varying duration were conducted to arrive at the final parameter set.

The resulting parameter set ñ used in the final simulation runs for the system-scale model ñ is given as Appendix 1. This set was also used for the intertidal mudflat model (Brooke *et al.*, 2006). The high TSS attenuation coefficient (1000 $m^{-1}(kg\ m^{-3})^{-1}$) and high CDOM attenuation coefficient for fresh water (5.4 m^{-1}) may be compensating for underestimated suspended solids concentrations in Fitzroy Estuary. Other points of interest in the calibrated parameter values are noted in the discussion.

Model verification (comparison with observations)

Tidal correction and contouring of observational data

In preparation for comparisons between model output and observational data and preparation of nutrient budgets, some pre-treatment of observational data was required.

Field samples taken during each of the three campaigns (September 2003, August 2004 and February 2005) were analysed to determine nutrient concentrations as described by Radke *et al.* (2006). Sample sites covered the Fitzroy Estuary, Keppel Bay and Casuarina Creek; however, it was not possible to take all measurements at exactly the same time. A consequence is that simply contouring the water quality observations at the observed locations will not provide an accurate snapshot of the distribution of material in the bay, since a given parcel of water in Keppel Bay may move 20 km between high tide and low tide (Figure 7).

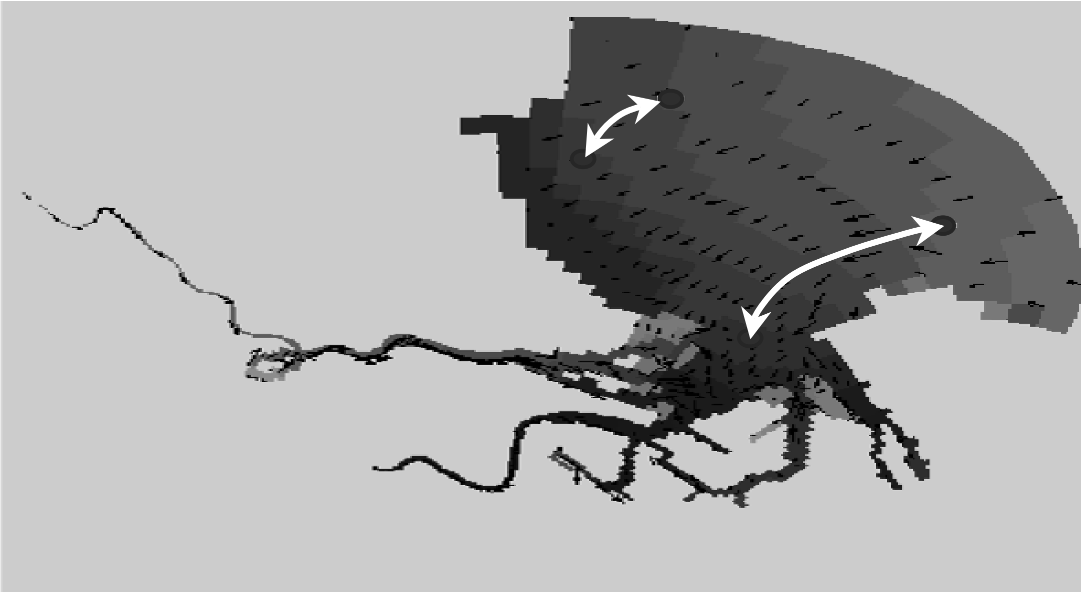

Figure 7. Approximate paths of two parcels of water in Keppel Bay between high and low tides on a spring tide (white arrows)

Black arrows indicate the direction and magnitude of surface currents simulated by the hydrodynamic model.

To allow a better snapshot of conditions at mean tide, the locations of observations during dry season campaigns were tidally ëcorrectedí. In other words, each sample was associated with a parcel of water, and we estimated the location of each parcel at the first mean tide following the actual time of observation. To arrive at this estimate, the hydrodynamic model was run with output at 15-minute intervals throughout the duration of each field campaign.

The estimated water velocity at the surface was used to track the movement of each parcel in 15-minute increments until surface elevation at the location of the water parcel passed the mean surface elevation. The latitude and longitude of a water parcel at this point were associated with the measured nutrient concentration from that sample.

Tidal correction was not attempted for the wet season (February 2005) field campaign because the strength of freshwater currents was at times equal to or greater than tidal currents and this could result in distorted contours.

Concentrations of nutrients were interpolated between corrected observation locations using a standard linear interpolation with a mask applied to prevent concentrations inside Fitzroy Estuary from influencing contours along the coast to the north. Concentrations outside the range of observation locations were extrapolated using the ënearest neighbourí method.

This method corrects for tidal movements of water parcels, but cannot take into account the significant effects of resuspension and deposition of particulate material over the course of the tidal cycle, nor the effects on dissolved oxygen and chlorophyll *a* of diurnal fluctuations in primary production.

Dry season (August 2004 comparison)

In general terms, model output for the dry season agrees well with the observational data from the two dry-season field campaigns (August 2004 and September 2003). Figures 8 to 17 compare contoured surface nutrient concentrations based on field observations (left) with model output (right) during the August 2004 field campaign. Crosses indicate the tidally corrected locations of field observations.

The model reproduces the observed range of total nitrogen concentrations very well (Figure 8). Concentrations in outer Keppel Bay are somewhat underestimated, reflecting the constant boundary conditions for nutrient concentrations, which were lower than observed conditions during this field campaign. Unfortunately, there were insufficient data to allow a temporally varying boundary concentration. Nitrogen concentrations in the inner bay, estuary and coastal creeks agree well with the available observational data, although it should be remembered that no observations were made in Connor Creek, Deception Creek or The Narrows, and contoured concentrations in these areas are extrapolated from concentrations in the inner bay.

The simulated range in total phosphorus concentration is also in reasonable agreement with observations (Figure 9), although total phosphorus appears to be slightly underestimated near the mouth of the estuary and coastal creeks. The model results suggest that tidally averaged total phosphorus and nitrogen concentrations and the distribution of these nutrients within the Fitzroy Estuary and Keppel Bay remain fairly consistent throughout the dry season, although concentrations vary strongly between the mouth of the estuary and the relatively ëblue waterí of outer Keppel Bay, and vary strongly over the course of each tidal cycle. This is consistent with the field observations, which found similar concentrations and spatial patterns in September 2003 and August 2004.

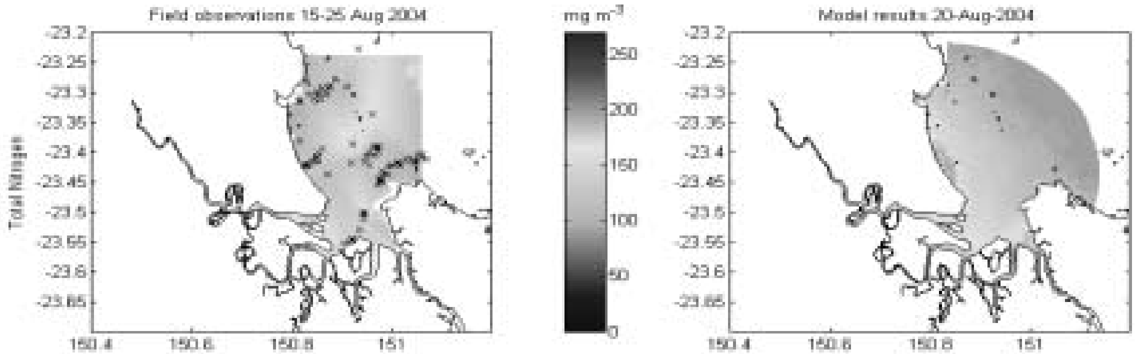

Figure 8. Total nitrogen from field data (left) and from model output (right), August 2004

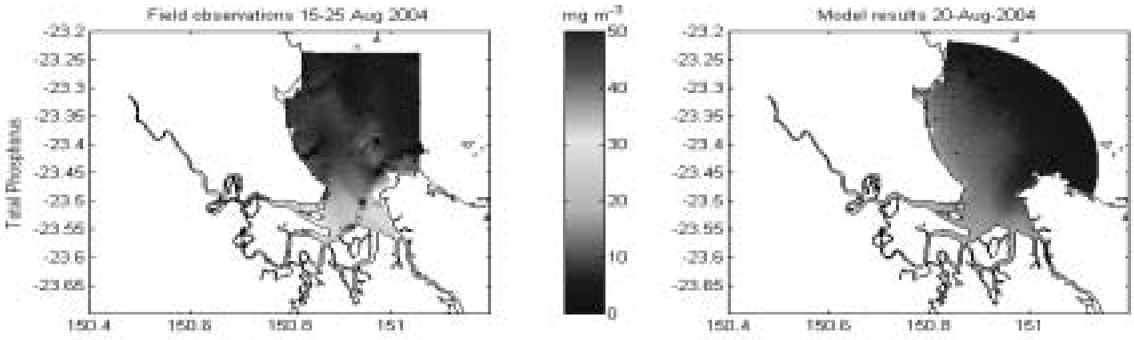

Figure 9. Total phosphorus from field data (left) and from model output (right), August 2004

Simulated total nitrogen and phosphorus concentrations along the coast from the Fitzroy Estuary towards Yeppoon are higher than suggested by the observations in August 2004, and were consistently elevated compared to offshore throughout the simulation. Further analysis indicates that this is due to high detrital nitrogen and phosphorus concentrations in this region, with detrital material resuspended in the shallow area near the coast and washed inshore with the rising tide. Initial conditions for sediment nitrogen concentrations were shown in Figure 3 (page 11). The region of elevated sediment nutrients around 150.85^{o}E, 23.4^{o}S is the source of the elevated water-column detrital nutrients near the coast in the simulation. It seems likely that the extent of this high-nutrient sediment patch is substantially overestimated in the interpolated sediment nutrient concentration field and that simulated nutrient concentrations along this part of the coast are too high as a result. Although this could be ëcorrectedí by adjusting the initial sediment conditions in line with this hypothesis, it is preferable to rely on the observational data available.

This issue highlights the sensitivity of the model to sediment nutrient concentrations. Early model runs, conducted with uniform initial sediment nutrient concentrations before the analysis of field data had been completed, were unable to reproduce even in general terms the observed spatial patterns in water column total nitrogen or total phosphorus.

Simulated dissolved organic nitrogen (DON) concentrations of around 100 mg N m^{-3} agree well with average observed concentrations; however, the model appears to underestimate the degree of spatial variability in DON (Figure 10). This may indicate that the pool of dissolved organic nitrogen is more biologically active than assumed in the model. Radke *et al.* (2006) suggests that DON in Keppel Bay is directly taken up by phytoplankton, which the model does not currently allow. Conversely, the apparent degree of spatial variability on the scale of the model domain in the observational data may be overestimated due to the effects of small-scale patchiness and outliers among samples. Figure 11 illustrates the effect of removing a single outlying data point on the contour map.

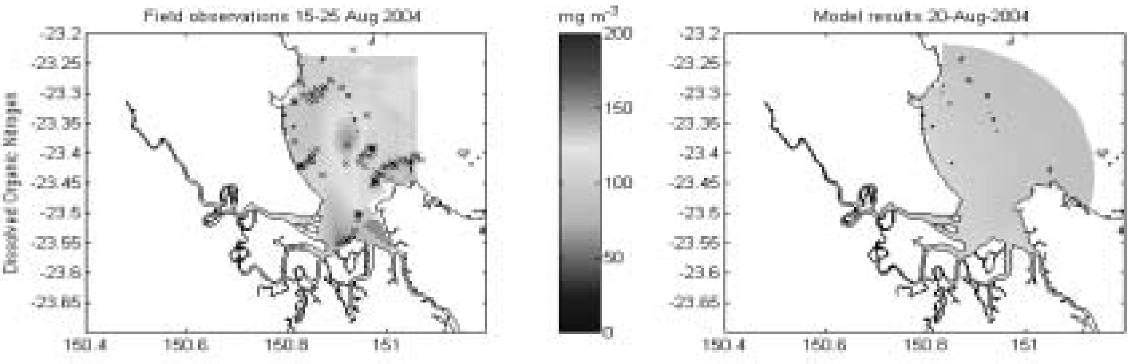

Figure 10. Dissolved organic nitrogen from field data (left) and from model output (right), August 2004

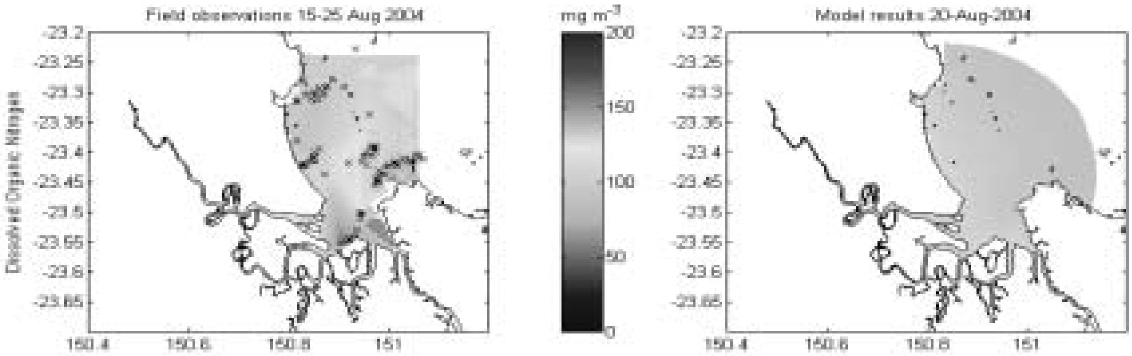

Figure 11. Dissolved organic nitrogen from field data (left) and from model output (right), August 2004, omitting a suspect data point at (150.92°E, 23.38°S)

Simulated dissolved inorganic nitrogen (DIN, Figure 12) and chlorophyll *a* (Figures 13 and 14) are in reasonably good agreement with observational data, although the model overpredicts chlorophyll along the coast between the Fitzroy Estuary and Yeppoon (perhaps due to the overestimated nutrient concentrations in this region), and may underestimate chlorophyll in the south-east (remembering that no observational data are available near The Narrows and Deception Creek). The low concentrations in outer Keppel Bay again reflect the use of a constant open boundary condition. We anticipate that remote sensing of chlorophyll *a* and other water quality variables will provide a solution to this problem in the future.

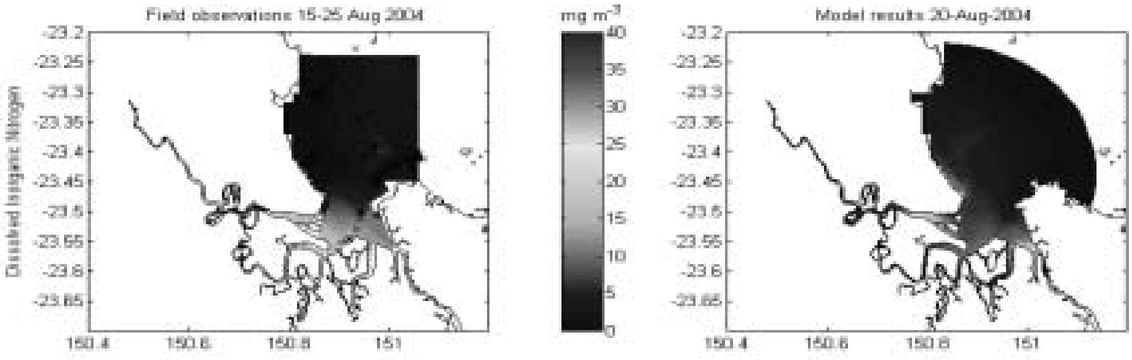

Figure 12. Dissolved inorganic nitrogen from field data (left) and from model output (right), August 2004

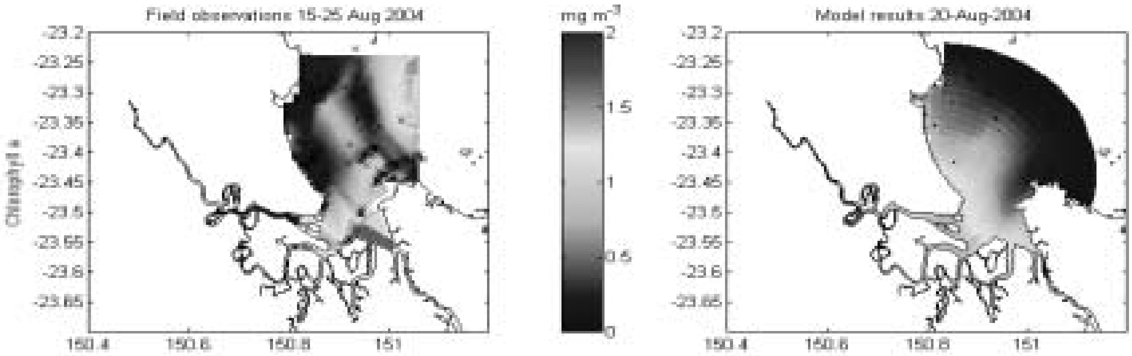

Figure 13. Chlorophyll *a* from field data (left) and from model output (right), August 2004

The pattern of chlorophyll *a* in the upper right of the left map is an artefact of the contouring method used.

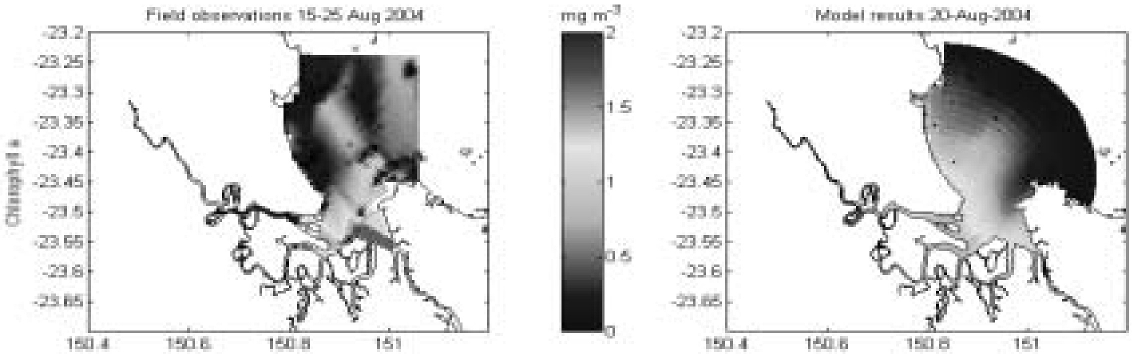

Figure 14. Chlorophyll *a* from field data (left) and from model output (right), August 2004, omitting a suspect point at (151.02°E, -23.34°S)

Interestingly, the model appears to slightly underestimate DIP (Figure 15) and slightly overestimate DOP (Figure 15). This may indicate insufficient uptake of DOP relative to DIP by *Trichodesmium* in the model.

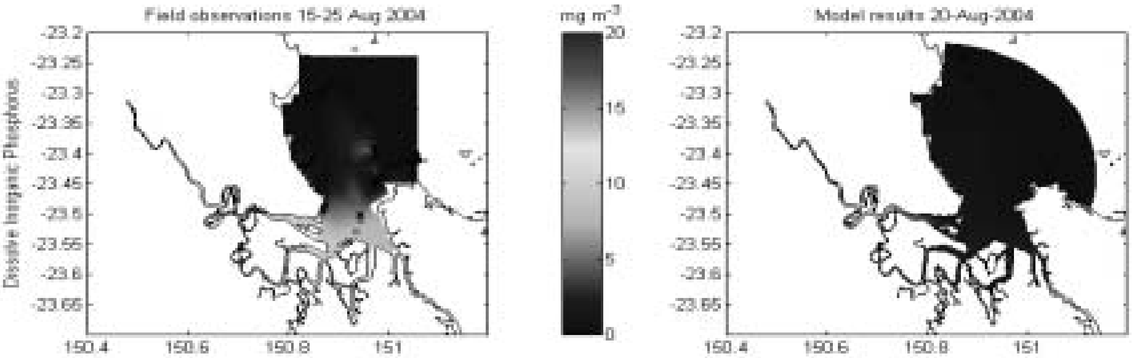

Figure 15. Dissolved inorganic phosphorus from field data (left) and from model output (right), August 2004

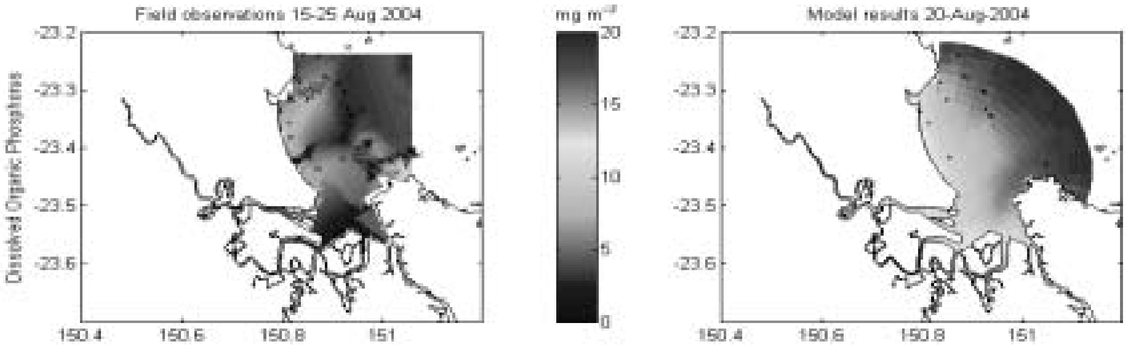

Figure 16. Dissolved organic phosphorus from field data (left) and from model output (right), August 2004

Dissolved oxygen (DO) was near saturation throughout Keppel Bay in both the model and observational data (Figure 17). Again, the impact of constant boundary conditions is shown in the deviation of simulated concentrations near the outer boundary from observed DO. The model appears to overestimate DO in some areas, perhaps reflecting underestimation of community respiration by biota, with only primary producers and zooplankton represented in the model.

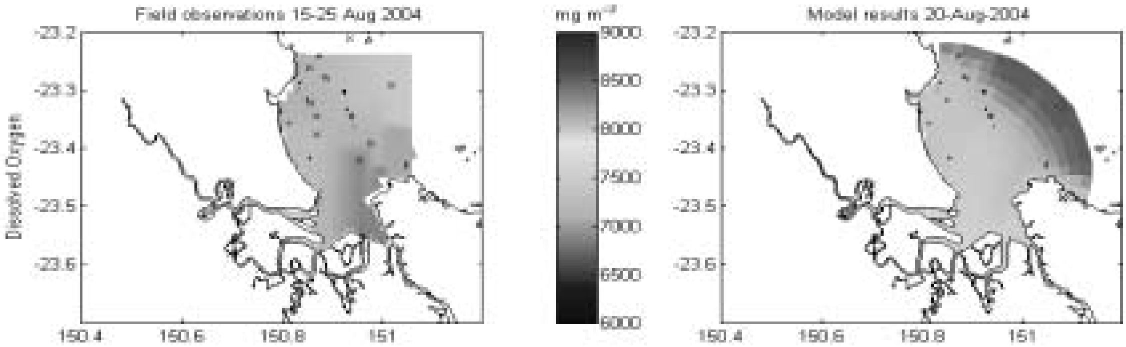

Figure 17. Dissolved oxygen from field data (left) and from model output (right), August 2004

Time-series observations of water column nutrient concentrations were conducted at six sites over 12-hour periods during the August 2004 field campaign. Figures 18 to 21 compare model predictions with observational data at each of these sites. In general, the model overpredicts nutrient concentrations at station B (along the coast near Yeppoon) for reasons discussed above, but otherwise reproduces observed spatial patterns in concentrations of all TN, DIN and DON well. As mentioned above, DIP and TP are underpredicted and DOP overpredicted at stations F and G, in the inner bay, but are predicted well at other sites.

The model shows less temporal variability in nutrient concentrations at these stations on this timescale (Figure 22). This is probably due to the limited spatial resolution of the model, with grid cells around 500 m^2 in the inner bay and >1 km^2 in outer Keppel Bay, which limits spatial patchiness. Temporal variations in chlorophyll *a* may also relate to diurnal variations in production and respiration, which the model (with only daily light as input) cannot reproduce. Daily variations in photosynthetic production are discussed by Radke *et al.* (2006).

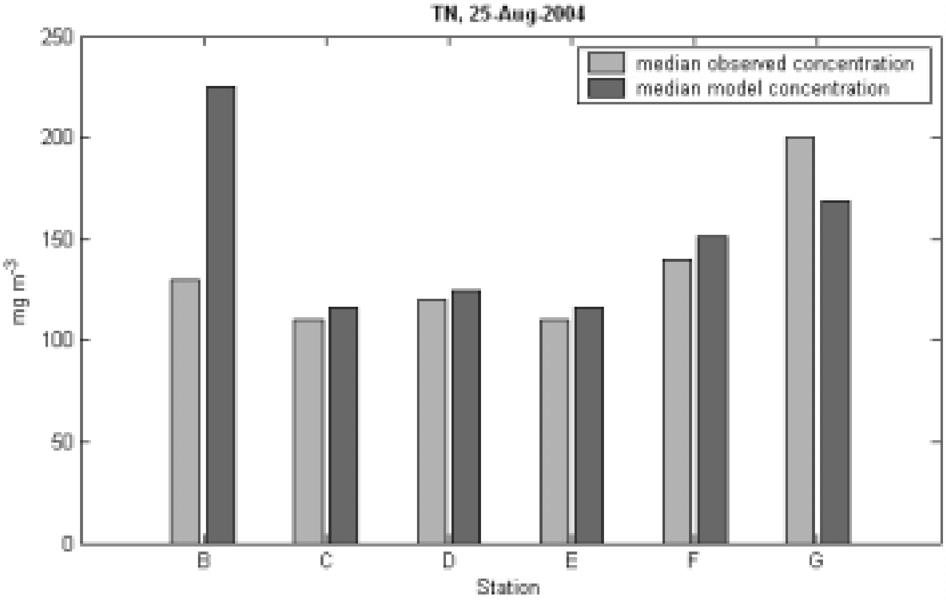

Figure 18. Median observed and simulated TN concentrations over a 12-hour period

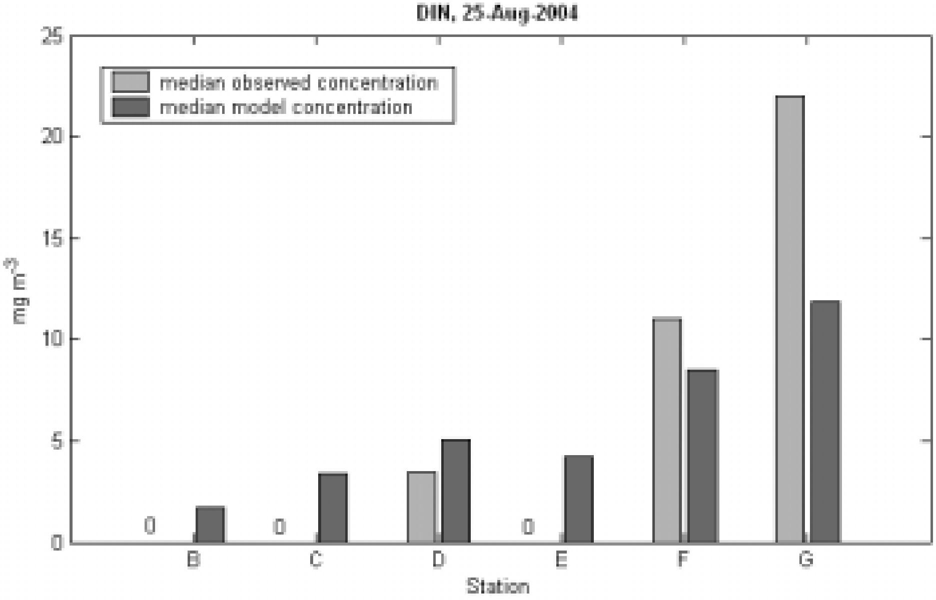

Figure 19. Median observed and simulated DIN concentrations over a 12-hour period

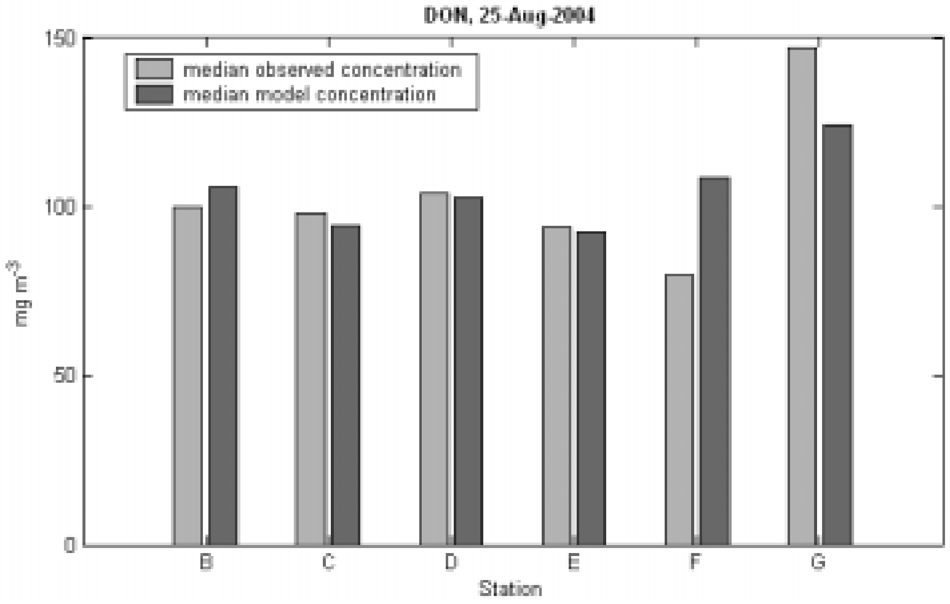

Figure 20. Median observed and simulated DON concentrations over a 12-hour period

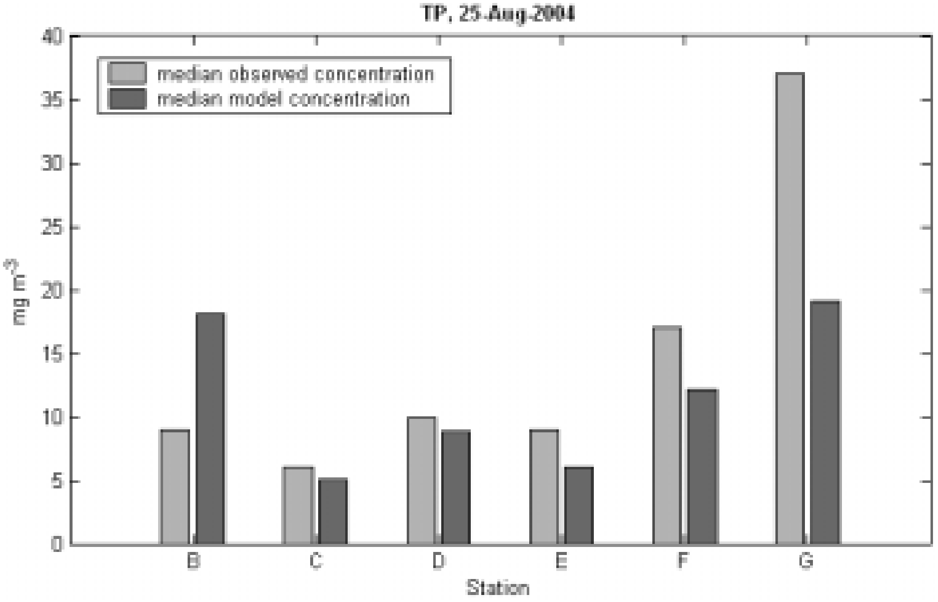

Figure 21. Median observed and simulated TP concentrations over a 12-hour period

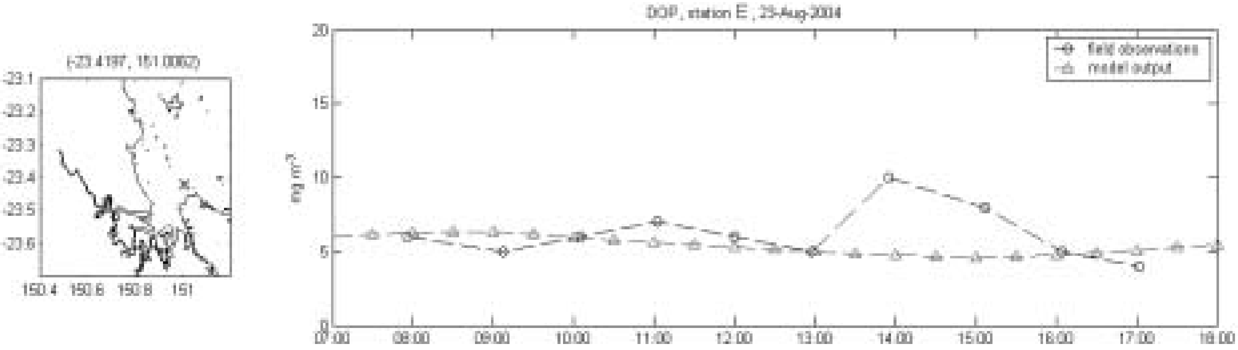

Figure 22. Simulated and observed DOP concentration at station E over an 11-hour period

The model predicts significant growth of microphytobenthos (MPB) in the shallow areas of the coastal creeks and along the western coast (Figure 23). The model does not take into account the impact of shading and nutrient uptake by mangroves, which may have a substantial impact on actual microphytobenthos concentrations in the creeks. The occurrence in the simulation of MPB in the mouth of the estuary in the simulation is surprising given the high turbidity in this region, and may reflect growth in the very shallow, tidally exposed areas near the mouth, and subsequent deposition. The model does not represent the bathymetry of the extensive intertidal mudflats on the fringes of the system because of insufficient spatial resolution, so there was a need to also implement the more focused intertidal mudflat model, which is described in Report 47 (Brooke *et al.*, 2006).

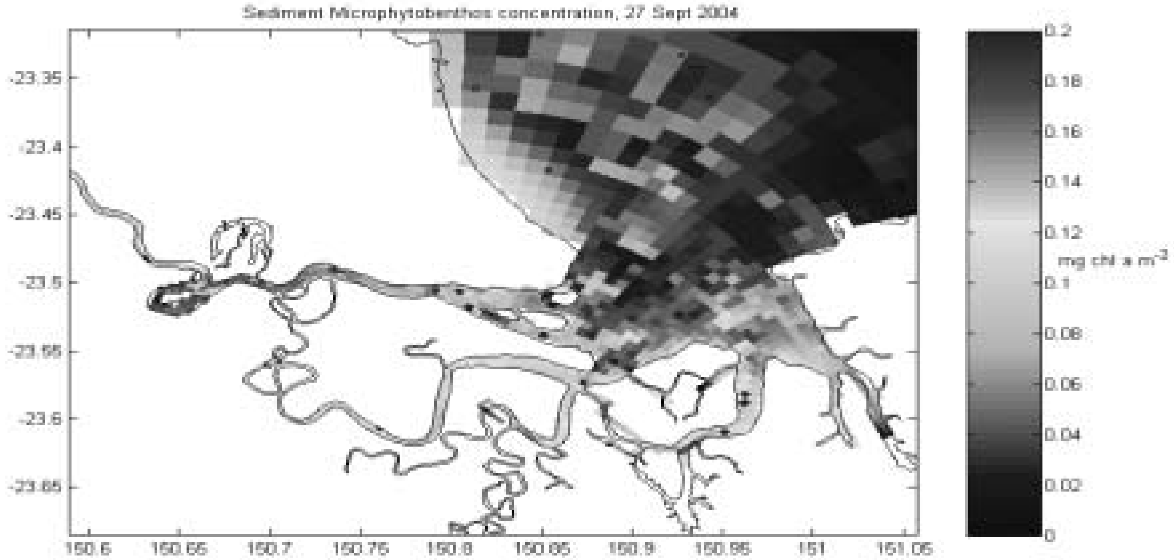

Figure 23. Simulated sediment microphytobenthos concentration on a system scale

Intertidal mudflats are not well represented on this scale.

Wet season (February 2005 comparison)

Model results for the wet season (February 2005) agree less well with field observations. Figures 24 to 31 present comparisons of field observations with model output for the February 2005 field campaign. The range and distribution of simulated concentrations of DIN (Figure 26) and DIP (Figure 29) in Keppel Bay in February 2005 are acceptably close to observed values, and predicted chlorophyll *a* (Figure 31) and DOP (Figure 30) concentrations are reasonable, though not a precise match to observations. As in August 2004, DOP along the coast towards Yeppoon is somewhat overestimated by the model - the reasons for this are as discussed above.

More serious departures are evident in total nitrogen (Figure 24), total phosphorus (Figure 28) and dissolved organic nitrogen (Figure 27) concentrations, which are substantially underpredicted by the model during February 2005. This indicates that the model is significantly underestimating the amount of particulate and organic nutrient material present in Keppel Bay during this period. Anecdotal observations as well as model results (Figure 25) indicate that conditions change rapidly in the wake of a major flow event. Even ëtidally correctedí field observations may not represent an accurate snapshot of field observations. Nonetheless, simulated TN concentrations in Keppel Bay barely exceeded 300 mg N m^{-3} at any time over the resolution of the flow event, whereas observed TN exceeded 500 mg N m^{-3} in the inner bay and approached 900 mg N m^{-3} in the mouths of the tidal creeks (Figure 24). There are two or three probable explanations for this discrepancy.

The concentrations of nutrients in the freshwater inflow derived from a regression of TN and TP against flow rate in previous years (over a predominantly dry period) may not adequately reflect nutrient concentrations in February 2005. Similarly, the assumption of constant DON concentrations may not be appropriate during this period. To improve these assumptions it would be necessary to either use direct measurements to force the inflow boundary conditions or to use a catchment model capable of simulating daily changes in nutrient concentrations in freshwater inflows. Most catchment models have not yet reached the point where this can be done reliably.

Characteristics (such as particle size, settling rates and decay rates) of particulate nutrients in fresh flows from the catchment may differ substantially from those of particulate nutrients in established sediments and may not be adequately described by a model that uses fixed parameter values to define these rates.

The very high concentrations shown in the field data contours over most of the inner bay and towards The Narrows are heavily influenced by a small number of observation points located (for logistical reasons) very close to the shore (Figure 24). These points may or may not be representative of the whole region affected. Similarly, the elevated TN concentration shown in the north-east of Keppel Bay in the field observation contour map is due to the influence of a single data point.

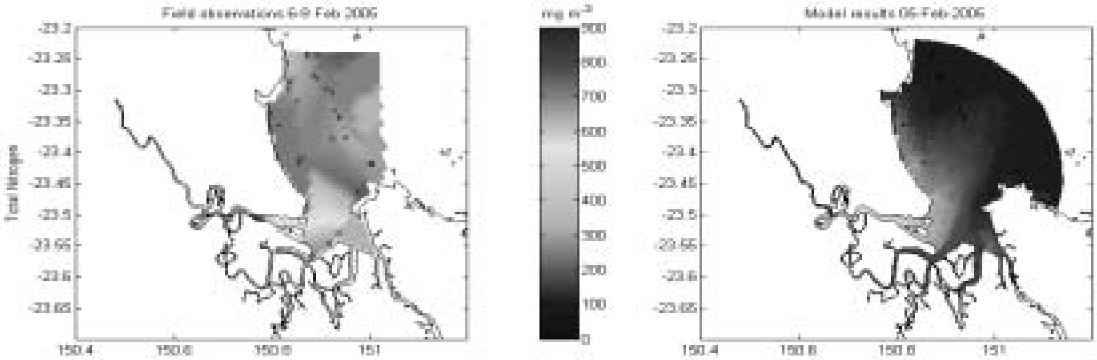

Figure 24. Total nitrogen from field data (left) and from model output (right), February 2005

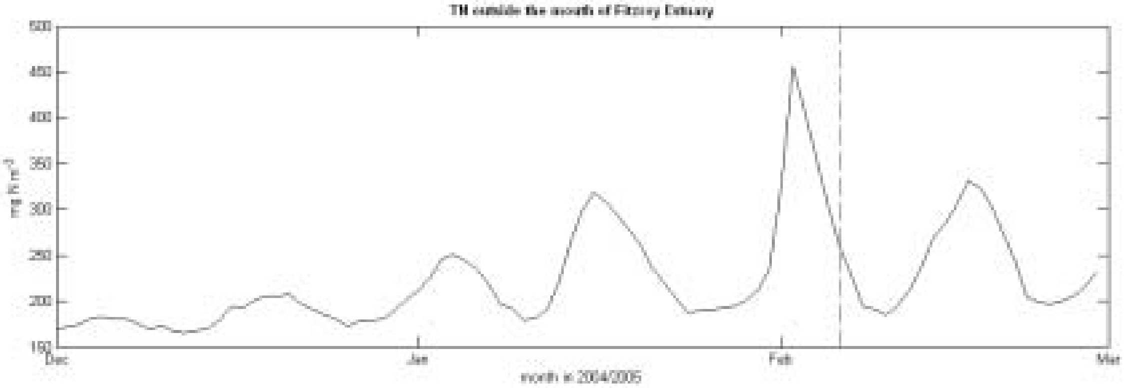

Figure 25. Time series of simulated total nitrogen concentrations near the mouth of Fitzroy Estuary

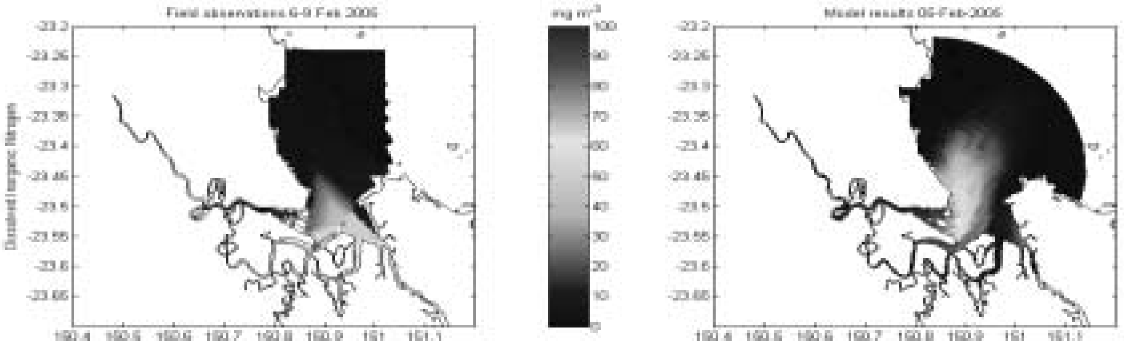

Figure 26. Dissolved inorganic nitrogen from field data (left) and from model output (right), February 2005

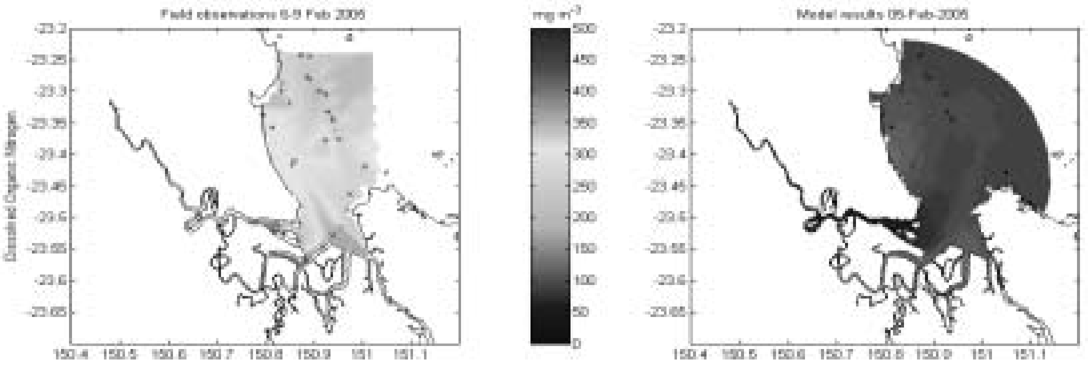

Figure 27. Dissolved organic nitrogen from field data (left) and from model output (right), February 2005

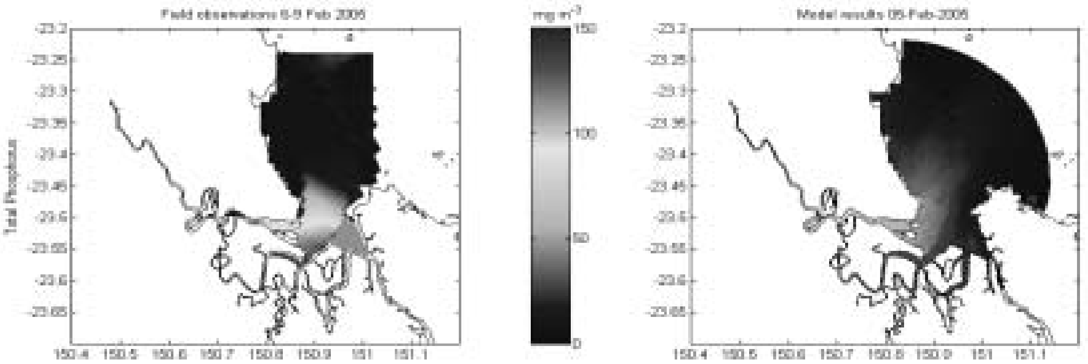

Figure 28. Total phosphorus from field data (left) and from model output (right), February 2005

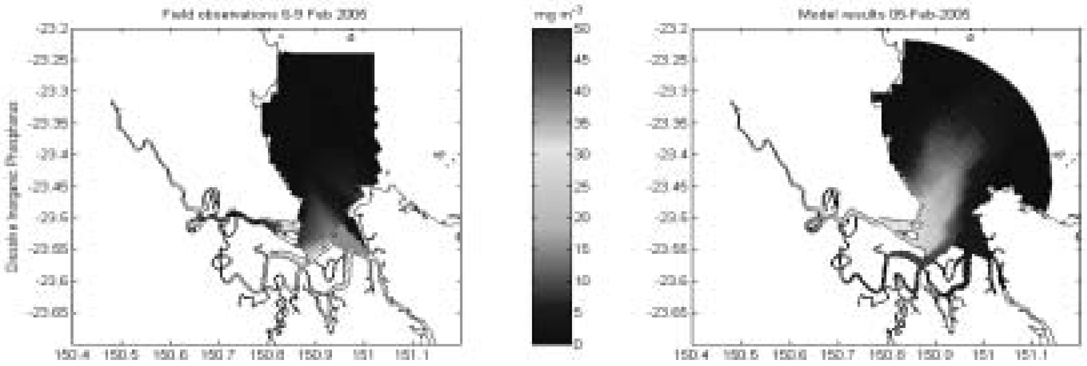

Figure 29. Dissolved inorganic phosphorus from field data (left) and from model output (right), February 2005

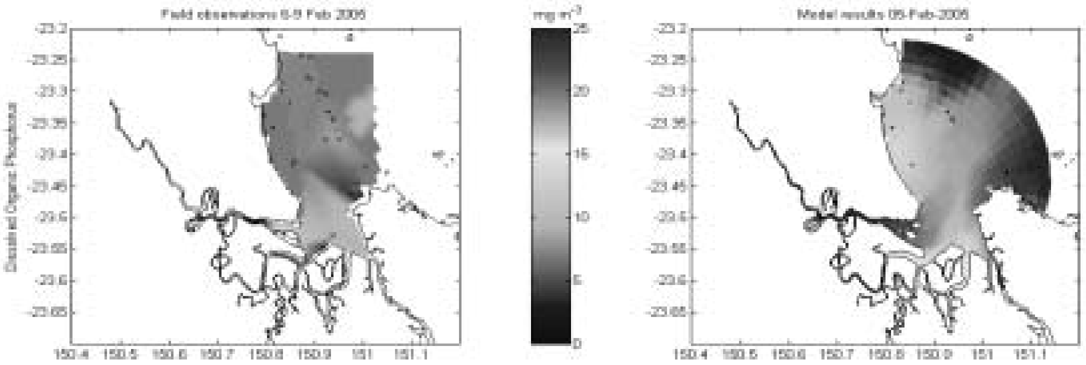

Figure 30. Dissolved organic phosphorus from field data (left) and from model output (right), February 2005

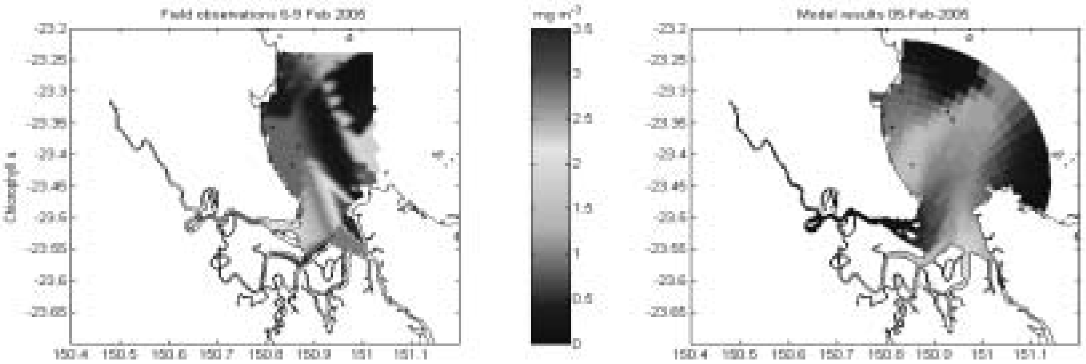

Figure 31. Chlorophyll *a* from field data (left) and from model output (right), February 2005

The angular patterns in the field contours are due to interpolation from a limited number of data points.

In summary, the wet-season model results for particulate and organic nutrients should be treated with caution and the model may tend to underestimate the export of nutrients to Keppel Bay during and immediately following freshwater flow events.

Chlorophyll *a*

Long-term monthly chlorophyll *a* monitoring is conducted by the Australian Institute of Marine Science (AIMS) at two sites within the model domain. A comparison between AIMS observations and model output is shown in Figure 32. The peak in October 2004 is due to *Trichodesmium* blown in from offshore, which the model could not reproduce with a constant boundary condition. These results show that simulated chlorophyll *a* concentrations in midñouter Keppel Bay are generally within the range of observations, but do not follow specific trends and underestimate peak concentrations.

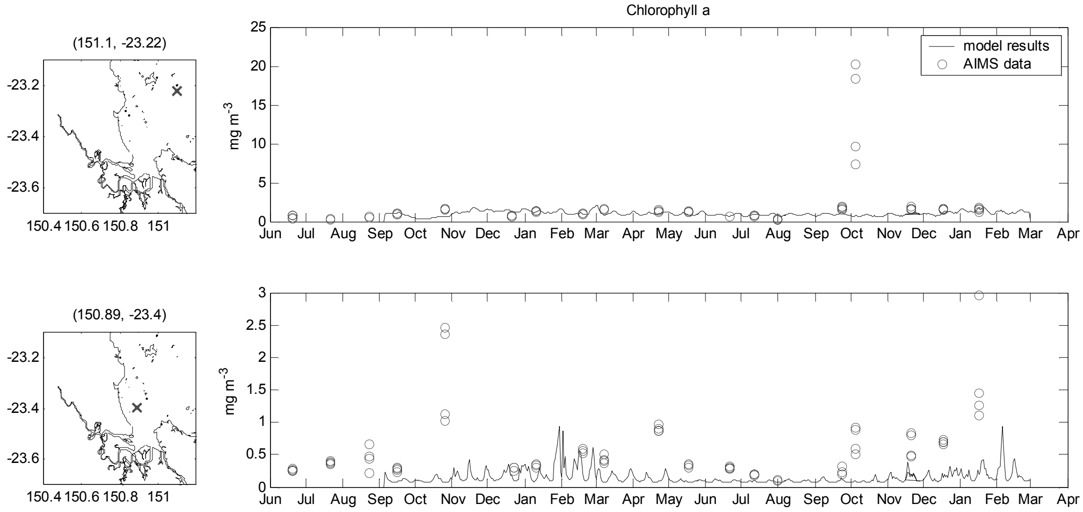

Figure 32. AIMS chlorophyll *a* data versus simulated chlorophyll *a* at nearby locations

Effect of variation in rainfall: high, low and median flow years

Not unexpectedly, simulated concentrations of nutrients and sediments vary greatly during and immediately following flow events of different sizes (Figure 33). In the median flow (calibration) year, TN concentrations had returned to pre-flow conditions by May, after which oscillations on a timescale of around two weeks reflected the spring-neap tidal cycle (higher TN and suspended sediment concentrations are associated with the stronger tidal currents of a spring tide). In the high flow year simulation (using flows from SeptemberñOctober 1998), nutrient and sediment concentrations were much higher at all sites during the wet season (i.e. December to May), and remained elevated until September (Figure 33). In the low flow year, nutrient and sediment concentrations remained close to pre-flow concentrations throughout the year.

In the analyses that follow, the ëwet seasoní is defined as December to April (the period during which the impact of freshwater inflows was most strongly evident in all three scenarios), and the ëdry seasoní is defined as May to November.

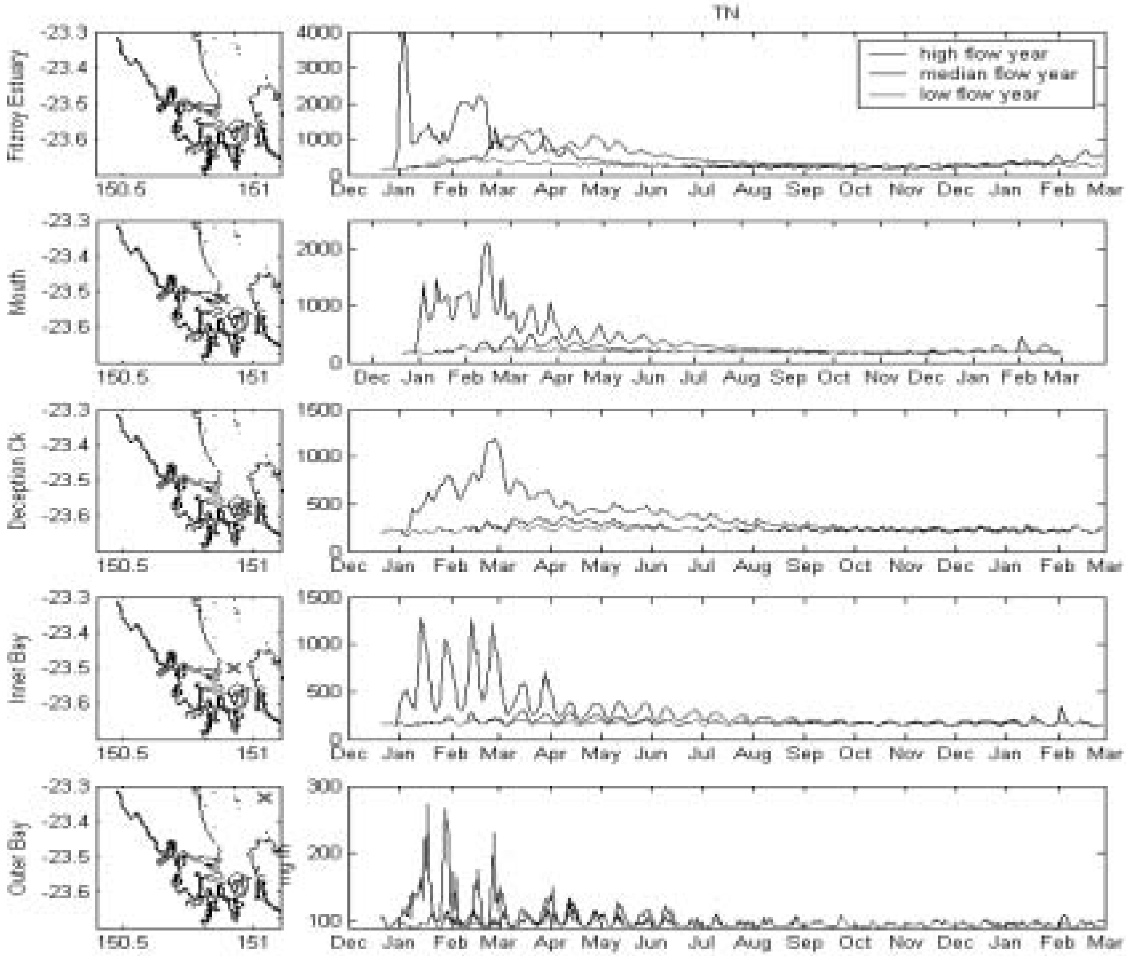

Figure 33. Changes over time in surface total nitrogen concentrations (mg N m^{-3}) at five sites, from daily model output

Loads of sediments, particulate nitrogen and particulate phosphorus to the Fitzroy Estuary vary in direct proportion to river flow in the model, and this is reflected in the differences between median TSS (Figure 34), TN (Figure 35) and TP (Figure 36) concentrations during the wet season, particularly in the estuary and inner Keppel Bay. Concentrations of particulate material are lower in the dry season, when relatively small amounts of fresh material are brought across the barrage from the catchment; however, the model predicts that the effects of sediment loads from flood events on water column suspended sediment and nutrient concentrations continue for several months following a flood event. Material deposited during the flood is available for resuspension in the months following, and will only be gradually depleted in the lead-up to the next flood. This is reflected in the differences between dry season TSS, TN and TP concentrations in the wet year, median year and dry year simulations (Figures 34 to 36).

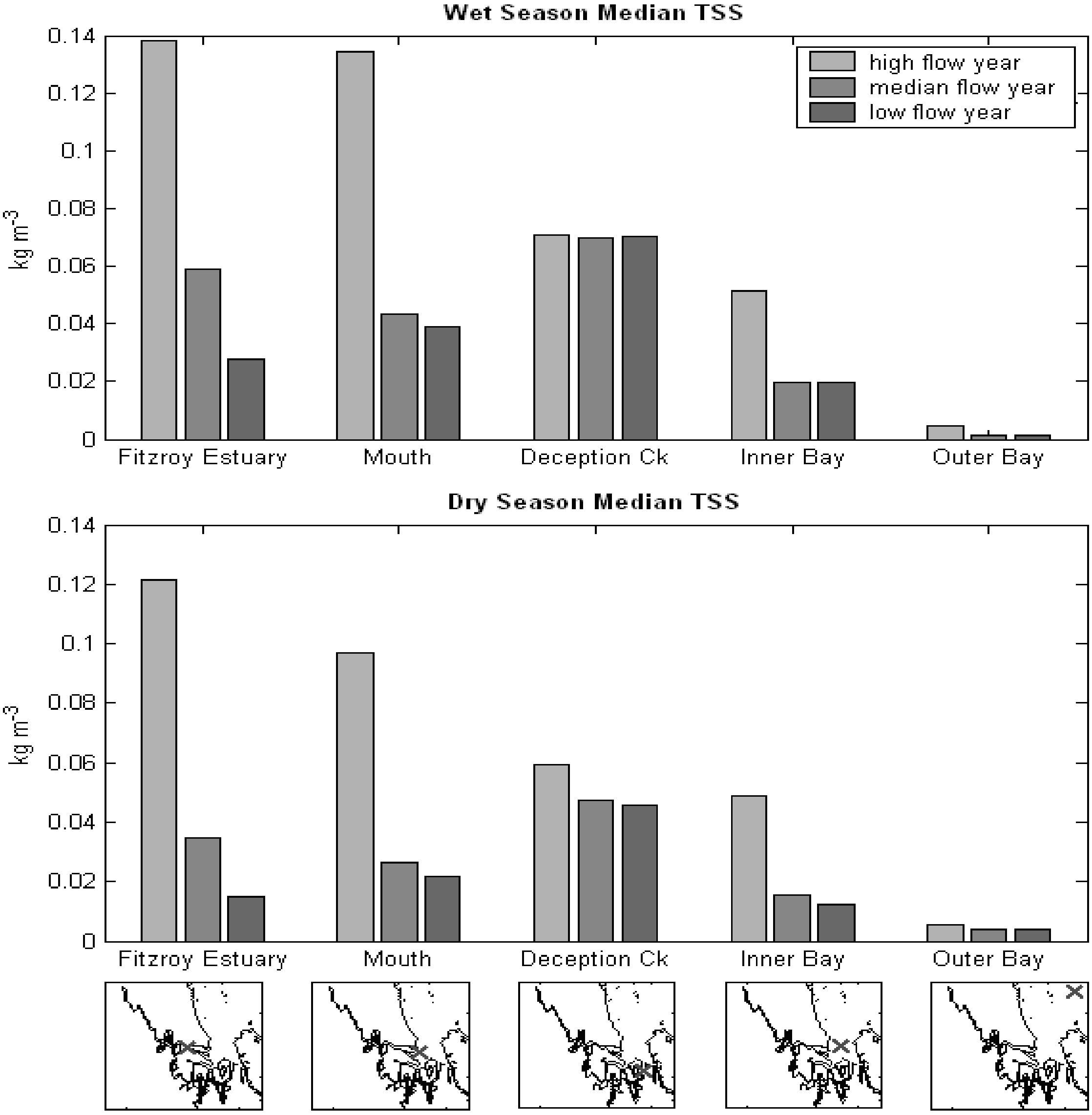

Figure 34. Median simulated total suspended solids concentrations at five sites during the wet season (top) and dry season (bottom) at five sites

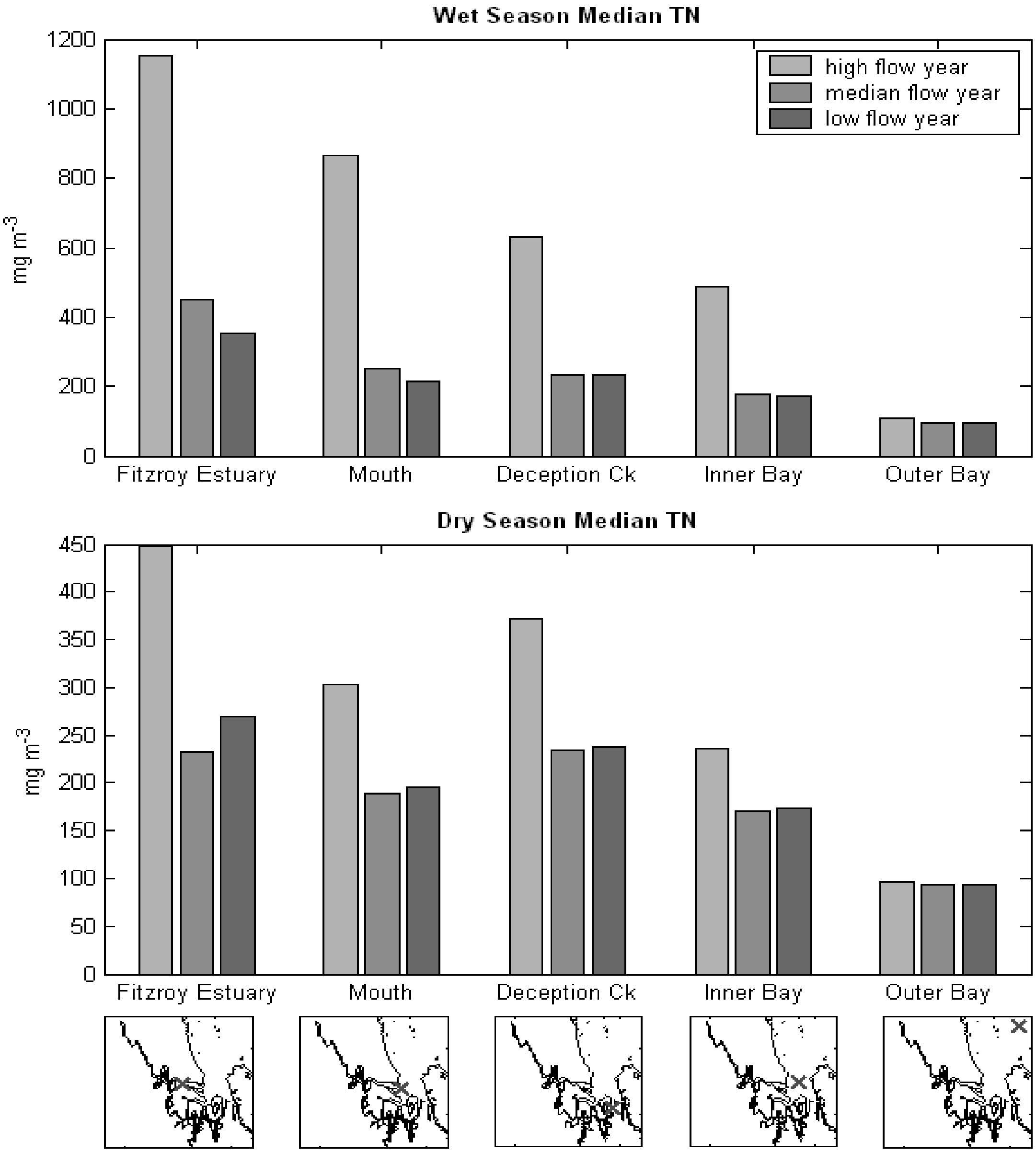

Figure 35. Median simulated total nitrogen concentrations at five sites during the wet season (top) and dry season (bottom) at five sites

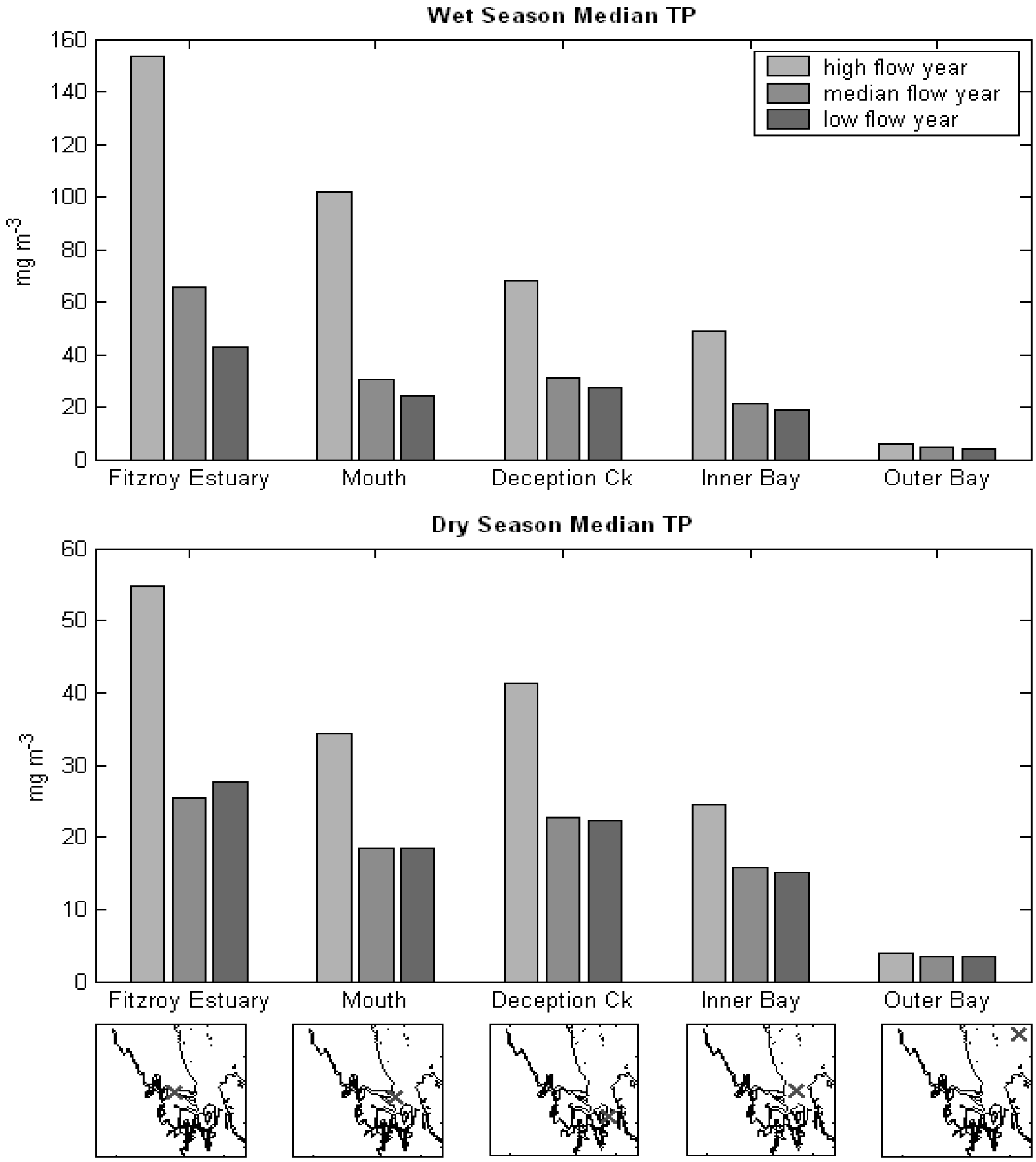

Figure 36. Median simulated total phosphorus concentrations at five sites during the wet season (top) and dry season (bottom) at five sites

The model predicts increased turbidity and hence lower pelagic primary production and lower chlorophyll *a* (Figure 37) both during the wet season and in the months following in a high flow year. In a lower flow year, wet season turbidity is slightly lower than in a median flow year and residence times are higher, allowing more time for growth of phytoplankton and slightly higher wet-season chlorophyll *a* concentrations (Figure 37). Predicted chlorophyll *a* concentrations in the dry season following a low flow summer were, however, predicted to be slightly lower than in the median flow year, possibly due to slightly lower concentrations of dissolved nutrients at the start of the season. Median DIN (Figure 38) and DIP concentrations for the dry season are, however, slightly higher for the low flow year than the median flow year, as concentrations recover later in the season.

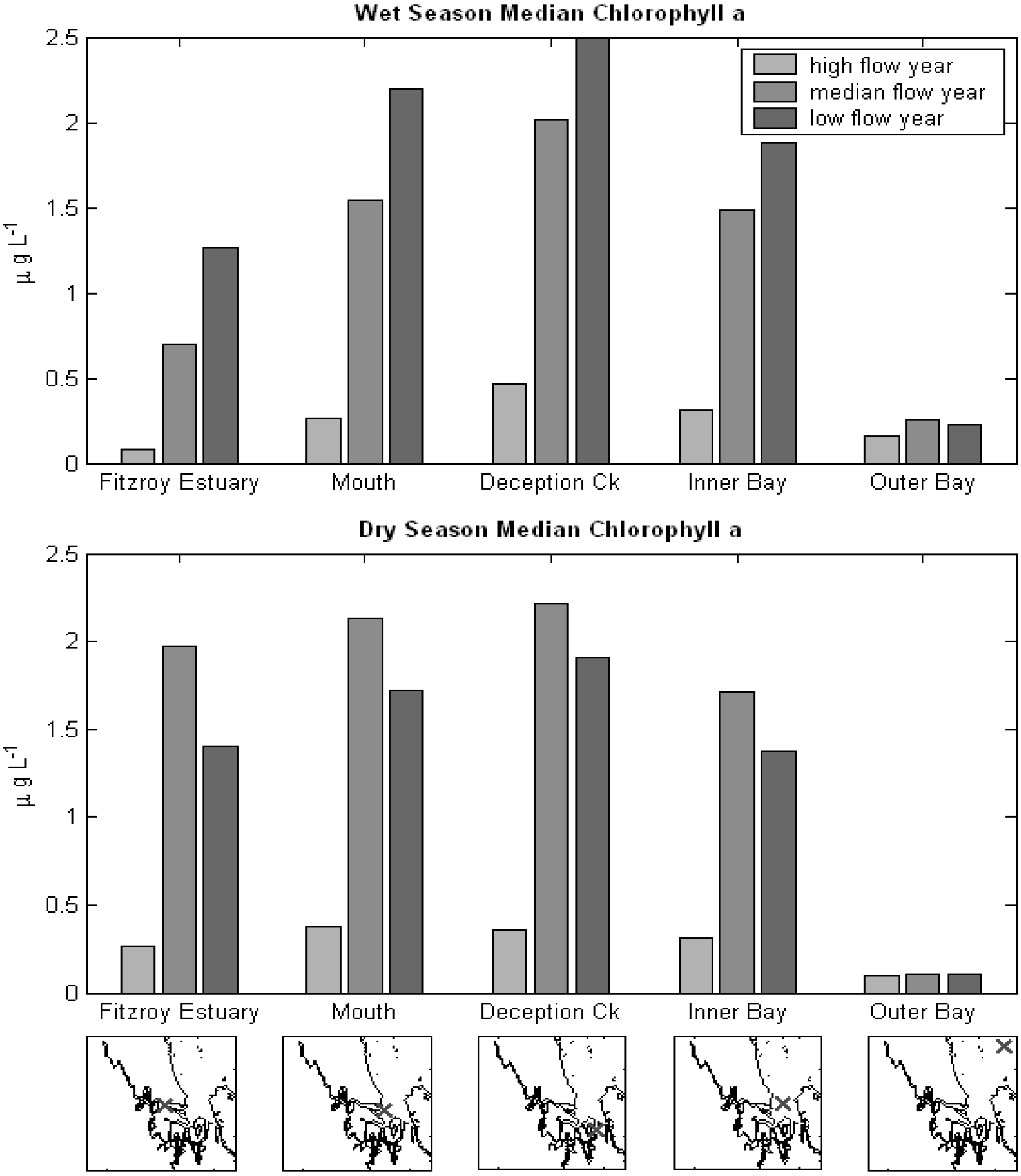

Figure 37. Median simulated chlorophyll *a* concentrations at five sites during the wet season (top) and dry season (bottom) at five sites

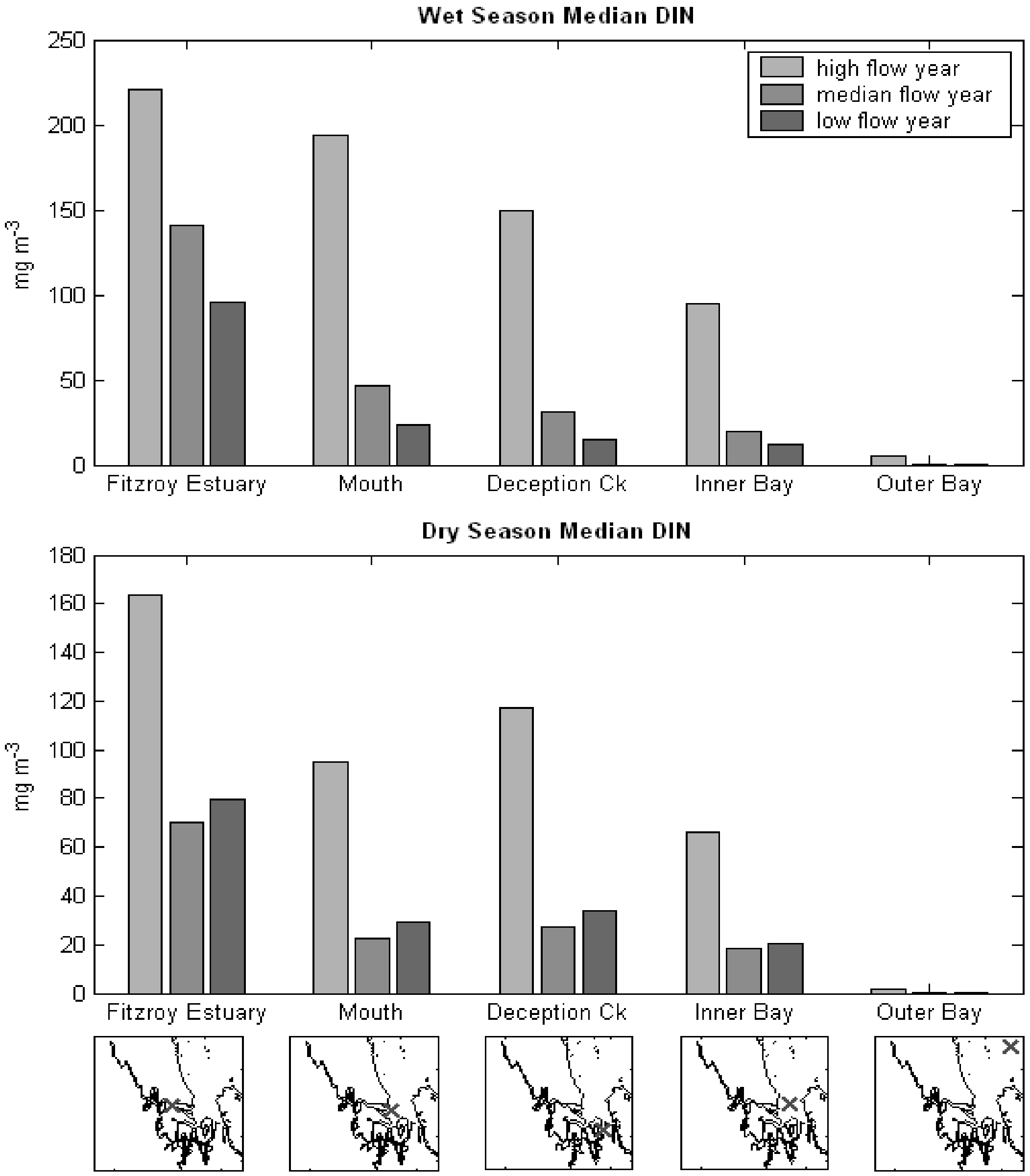

Figure 38. Median simulated dissolved inorganic nitrogen concentrations at five sites during the wet season (top) and dry season (bottom) at five sites

Nutrient budgets: Method

Two methods are available for calculation of nutrient budgets in this project. First, field observations of nutrient concentrations can be combined with exchanges calculated from the hydrodynamic model. Second, fluxes of nitrogen, phosphorus, carbon and suspended sediments across boundaries in the model can be calculated directly during model runs. The first approach has the advantage that it makes direct use of field data and does not rely on the accuracy and completeness of the biogeochemical model, but it has the disadvantage that it relies on interpolation between widely scattered field observations and a necessary assumption that the system has reached a quasi-steady state (i.e. that the rate of change of the system is relatively slow and that internal concentration distributions are in approximate balance with their fluxes). With the steady-state assumption, this approach can only be applied to short periods within sustained periods of negligible inflow (i.e. dry-season conditions). The second approach can be applied over longer periods and to wet-season as well as dry-season conditions.

Approach 1 (Field observations and hydrodynamic model)

The model domain was divided into 23 boxes, shown in Figure 39. The average concentration of each nutrient and the average salinity within each box during September 2003 and August 2004 were calculated from the interpolated concentrations in the tidally corrected contour maps (see page 17 for an explanation of the tidal correction method).

Rates of exchange (m^3 water d^{-1}) between each box and its neighbours were calculated from the three-dimensional hydrodynamic model and averaged over a two-month period during the dry season.

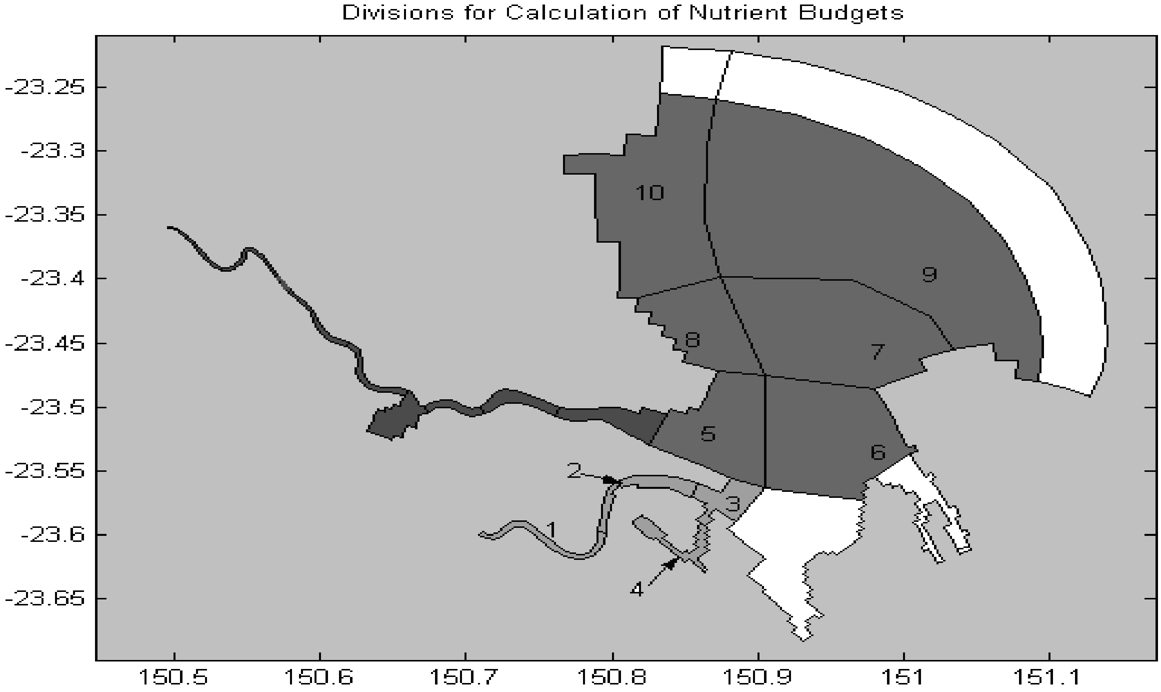

Figure 39. Boxes used in calculation of nutrient budgets from field observations

Boxes aggregated into the ëKeppel Bayí region are shown in blue, ëFitzroy Estuaryí in green, and ëCasuarina Creekí in orange.

We assume for this calculation that the system was at steady state at the time of the dry-season field campaigns, that is, that concentrations were not changing at the time of observation. Hence, the magnitude of the source or sink of any substance within a given box is given by the difference between the quantity imported from neighbouring boxes and the quantity exported to other boxes (Eqn 2).

$$s_i = \sum\nolimits_{n=1}^{m} \frac{(c_i + c_n)}{2} E_{n,i} - \sum\nolimits_{n=1}^{m} \frac{(c_i + c_n)}{2} E_{i,n} \qquad \text{(Eqn 2)}$$

where s_i is the source of material within box *i*, *m* is the number of neighbouring boxes, c_i is the concentration of material in box *i*, $E_{n,i}$ is the volume flux from box *n* to box *i* (m^3 d^{-1}), and $E_{i,n}$ is the volume flux in the other direction ($E_{i,n}$ and $E_{n,I}$ are equal if there is no net flow).

The estimated source or sink within each box during September 2003 and during August 2004 was calculated for each of: dissolved organic nitrogen (DON), dissolved organic phosphorus (DOP), dissolved inorganic nitrogen (DIN), dissolved inorganic phosphorus (DIP), particulate nitrogen (PN), particulate phosphorus (PP) and salinity. Any apparent source of salt in this calculation is due to evaporation, as biogeochemical processes do not significantly affect salinity. From the estimated salinity fluxes and observed daily rainfall, an implied rate of evaporation was calculated for each box. The estimated flux of each form of nitrogen or phosphorus in each box was then adjusted for evaporation.

For the purpose of reporting, results were aggregated for each of three regions. These are: Fitzroy Estuary, Keppel Bay (boxes 5ñ10, Figure 29), and Casuarina Creek (boxes 1ñ4). Results were not calculated for Connor Creek, Deception Creek or The Narrows, as insufficient field observations were available from the dry season field campaigns in these locations. Nutrient budgets for Fitzroy Estuary have previously been reported (Webster *et al.*, 2005), and the results are incorporated into this analysis.

Approach 2 (Biogeochemical model)

Fluxes of nitrogen across the outer boundary of the model were tracked over the course of each simulation. Daily model output was smoothed over a 28-day period to minimise tidal effects. From this smoothed data, daily exports and internal budgets were calculated.

Nutrient budgets: Results

Approach 1 (Field data plus hydrodynamic model)

The rate of evaporation calculated from the salt budget for September 2003 was 3.6 mm d^{-1}, and for August 2004, 4.5 mm d^{-1}. This compares well with an average estimated mean area potential evaporation rate of approximately 3.4ñ4.0 mm d^{-1} during AugustñSeptember shown on the Bureau of Meteorology web site (http://www.bom.gov.au/climate/averages/climatology/evapotrans/et.shtml), and allows first-order confidence in the budgets calculated with this method.

Results for all nutrient components are shown in Table 1.

Table 1. Dry season nutrient budgets calculated from field observations. Positive values indicate a source within the area indicated (or a net export, in the last column); negative values indicate a sink (or a net import)

		Fitzroy Estuary source ($t\ d^{-1}$)	Casuarina Creek source ($t\ d^{-1}$)	Keppel Bay source ($t\ d^{-1}$)	Export to GBR lagoon ($t\ d^{-1}$)
DON	Sept. 2003	-2.9	-0.03	0.38	-2.5
	Aug. 2004	-2.2	-0.29	-0.28	-2.7
DOP	Sept. 2003	-0.06	-0.03	0.02	-0.07
	Aug. 2004	-0.10	-0.02	-0.05	-0.17
DIN	Sept. 2003	-0.70	0.09	0.32	-0.05
	Aug. 2004	-0.72	0.00	0.49	0.01
DIP	Sept. 2003	-0.29	0.03	0.16	-0.08
	Aug. 2004	-0.20	-0.01	0.19	0.00
PN	Sept. 2003	-1.6	0.19	1.7	-0.05
(unreliable)	Aug. 2004	-0.85	0.03	0.37	-0.72
PP	Sept. 2003	-0.65	0.05	0.57	-0.02
(unreliable)	Aug. 2004	-0.36	0.00	0.33	-0.02

The budgets for particulate nitrogen and phosphorus calculated with this method are very unreliable given the strong tidal variability (and variability over depth) of particulate nutrient concentrations.

Results for the two dry-season field trips are surprisingly close, suggesting that conditions during September 2003 and August 2004 were very similar. Applying this approach using model output instead of field observations for August 2004 gives very similar results (e.g. DON export to GBR lagoon = -2.91 t N d^{-1}), reflecting the closeness of the match between observations and model predictions of water column nutrient concentrations during August 2004. The results for the Fitzroy Estuary ñ a net sink of approximately 4 to 5 t N day^{-1} ñ are also consistent with the results for May to December 2001 reported by (Webster *et al.*, 2005), who estimated a net sink of 20 t d^{-1} in the estuary, a figure not statistically distinguishable from zero given the variability of data.

Hence, both inputs of nitrogen and phosphorus to the Fitzroy Estuary and Keppel Bay and exports to the Great Barrier Reef lagoon during the dry season are very low. The budget suggests that there may be a small net loss of nitrogen and phosphorus from Keppel Bay during the dry season, countered by net accumulation during the wet season to produce the observed long-term net sediment accumulation over much of the Bay (Wild-Allen 2006, Report 36).

Approach 2 (Biogeochemical model)

Predicted total nitrogen fluxes using the model results directly are broadly comparable with the results from the field data and hydrodynamic model. For August 2004, the estimated total nitrogen export using Approach 1 was -3.46 t N d^{-1}; with Approach 2, the figure was -10 t N d^{-1}. The difference between the two numbers may be due partly to uncertainty in the export of particulate N in Approach 1.

Estimated TN budgets for the wet season (December to April) and the dry season (May to November) as well as the annual mean for each of the three flow scenarios are given in Table 2. The model predicts that the bulk of the total nitrogen load is retained within the system; indeed, the results for the median- and low flow years suggests that nitrogen may be imported from marine sources rather than exported to the Great Barrier Reef lagoon except during major flow events.

For the median flow year, the budget suggested a net accumulation of approximately 11 t N d^{-1} in the sediments of Keppel Bay. Observational data (Radke *et al.*, 2006; Wild-Allen *et al.*, 2006) indicates that there has been an average net accumulation of sediment material in inner Keppel Bay in the order of 77 t N yr^{-1} (approximately 0.2 t N d^{-1}) over the last 7000 years.

In the absence of regular monitoring data along the outer boundary, the model assumes a constant dissolved organic nitrogen concentration at the outer boundary of 90 mg N m^{-3}. There is some evidence from the field data, however, (Figure 10) that actual DON concentrations may vary significantly from this value. The model also appears to underestimate the spatial and temporal variability of DON in Keppel Bay and the tidal creeks. Hence, there is reason to doubt the DON component of the budget derived from the model results. In each of the three simulation years (representing a high flow year, a low flow year and a median flow year) the Approach 2 budget suggests a net import to Keppel Bay of approximately 5 t N d^{-1} as DON across the outer boundary. Approach 1 (using field observations) gives an estimated net import of around half this figure for September 2003 and August 2004 (Table 1). If we assume that Approach 2 overestimates import of DON by 2.5 t N d^{-1}, we arrive at an estimated annual TN export of approximately 5800 t N for the high flow year, -1800 t N for the median flow year, and -700 t N for the low flow year (compared with 4900, -2700 and -1600 t N respectively if we take the results of Approach 2 at face value).

Table 2. Total nitrogen budget from model results. ëWet seasoní results are for the period from December to April, ëDry seasoní, from May to November inclusive

		Load from catchment (t d^{-1})	**Internal sink (t d^{-1})**	**Export to GBR lagoon (t d^{-1})**
Low flow	Dry season	0.3	7.3	-7.0
	Wet season	2.5	2.3	0.2
	Annual mean	1.3	5.6	-4.3
Median flow	Dry season	0.3	8.9	-8.6
	Wet season	8.5	12.6	-4.1
	Annual mean	3.8	11.1	-7.3
High flow	Dry season	0.3	16.3	-16.0
	Wet season	62	21.6	40.4
	Annual mean	26	17	9.0

Discussion

Accuracy of the model

The model simulates dry-season concentrations of nitrogen and phosphorus (as DON, DOP, DIN, DIP, PN and PP) well. Simulation of wet-season conditions is reasonable, with some reservations: particulate nitrogen and dissolved organic nitrogen and phosphorus appear to be underestimated. This may be due to the difficulty of estimating inflow nutrient concentrations under high flow conditions or to overestimation of the rate of deposition of fresh particulate material in the Fitzroy Estuary. Sediment modelling results (Margvelashvili *et al.* 2006) found that total suspended solids were underestimated during high flow events. Possible reasons for this discussed in the report include insufficient data for prescribing the inflow boundary condition and gaps in our understanding of sediment processes. The same underlying model is used here to transport particulate nutrients.

The model is not able to capture changes in chlorophyll *a* due to *Trichodesmium* blooms blown in across the boundary from Keppel Bay, as observational data were not sufficient to provide temporally resolved open boundary conditions. Future integration of remote sensing data is a promising avenue to address this issue. Future development of a *Trichodesmium* model could also include the implementation of a surface film layer in the hydrodynamic model to allow better simulation of wind-blown surface blooms.

Uncertainties in the sediment model (Margvelashvili *et al.* 2006), which are considerable, carry through to the biogeochemical model results and uncertainties in the biogeochemical model itself add to these and should be kept in mind when evaluating the model results.

Breakdown of organic material in Keppel Bay

One very clear result from the model calibration is the suggestion that most of the particulate organic material in the system (and hence most of the total nitrogen and phosphorus) is not biologically available. This is indicated by the very low breakdown rate for refractory detrital material (0.00004 d^{-1}) required to reproduce observed nutrient concentrations, which suggests a half-life of approximately 47 years for organic sediments in Keppel Bay. This may in part reflect the high proportion of calcium-bound phosphorus observed in samples (Radke *et al.*, 2006), a factor not included in the model.

Despite the low rate of breakdown of organic material, the simulations showed a net consumption of inorganic carbon in Keppel Bay. This indicates that the system is net heterotrophic, even when respiration by biota at high trophic levels (e.g. fish) is not taken into account. In other words, the model suggests that biological processes in this system are driven more by the input of terrestrial carbon than by production of carbon by primary producers within Keppel Bay.

The results also suggest that particulate material brought into the system during freshwater flow events is less refractory and settles more slowly than material resuspended from established sediments. This is not surprising, as fresh material from the catchment has not yet been ëworked overí by aquatic bacteria that may rapidly take up the more bioavailable nutrients from particulates. Analysis of field results (Radke *et al.*, 2006) indicates that the nitrogen content of Keppel Bay muds (as a function of iron as a proxy for sediment surface area) is significantly lower than that of catchment soils, indicating that 70% of the original nitrogen content of soils has been lost from material incorporated into the sediments.

Primary production

Pelagic and benthic primary production are strongly light-limited in the mouth of the estuary, and phytoplankton and microphytobenthos growth in the model are therefore very sensitive to turbidity and to light absorption parameters. The relatively low calibrated absorption coefficients for phytoplankton cells (large phytoplankton, 1.0×10^4 m^{-1}, small phytoplankton, 1.5×10^4 m^{-1} and *Trichodesmium*, 1.5×10^4 m^{-1}) suggest that the dominant phytoplankton in the area are adapted to the high solar irradiance typical of tropical climates rather than to the highly turbid conditions near the mouth of the estuary, to which they have a relatively short exposure. By contrast, microphytobenthos appear to have a high absorption coefficient (7×10^4 m^{-1}), reflecting the low light habitat of sublittoral benthic algae. Intertidal mudflats are exposed to higher light not well represented in this broadscale model.

The sensitivity of primary producers to turbidity suggests that catchment changes that result in a change in sediment loads (and hence turbidity) are likely to have a significant effect on production within the system as well as exports to the Great Barrier Reef.

Interestingly, chlorophyll *a* concentrations were found to be sensitive to zooplankton grazing parameters, suggesting that top-down control of primary production is important in this system.

Nitrogen budget

The average nitrogen budget over all three years (wet, dry and median flow) is summarised in Figure 40. The results of the total nitrogen budget are consistent with evidence of net sediment nitrogen accumulation from the sediment data (Radke *et al.*, 2006). The estimated results for DON, however, illustrate the high degree of uncertainty in the budget estimates, which may be out by 50ñ100%. Further monitoring to refine boundary conditions for dissolved organic material and further validate treatment of dissolved organic nutrients in the model is advisable.

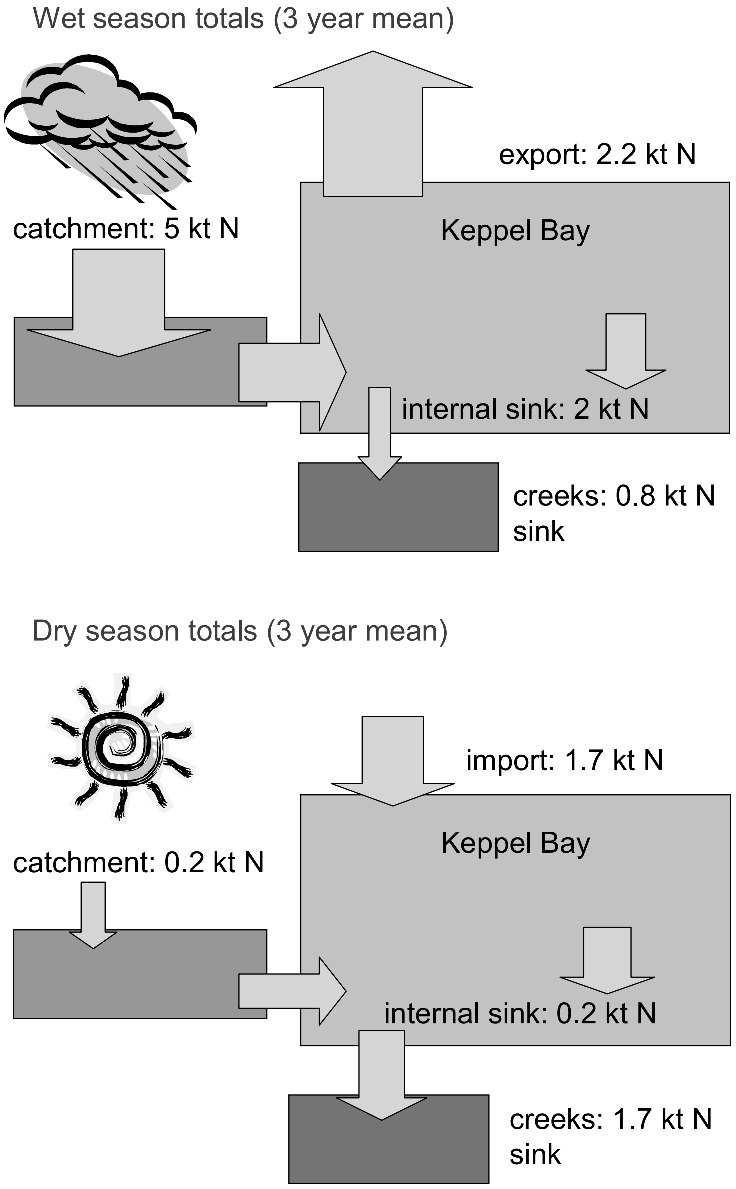

Figure 40. Wet (top) and dry season (bottom) nitrogen budget summaries for a median flow year. Figures do not add up to zero because of rounding

The model does not show nitrogen fixation to be a significant factor in the nitrogen budget and, in this respect, it does not accord with the evidence for nitrogen fixation found in the field data (Radke *et al.*, 2006).This may represent a failure of the model to accurately simulate the extent of benthic nitrogen fixation.

The model suggests that there may in many years be a net import of nitrogen from marine sources, although there is a net export during high flow years. This result is surprising and may change if further data become available.

High flow versus low flow years

There is a very substantial interannual variability in rainfall and hence flows and loads in the region. In a high flow year, the wet season lasts longer and the impact of flow events on water column sediment and nutrient concentrations is evident over a larger area of Keppel Bay and for a longer time than in a median or low flow year. The efficiency with which material is transported through the Fitzroy Estuary and Keppel Bay varies considerably and depends on flow volumes and current velocities. In our simulations, the total nitrogen load in the high flow year was seven times higher than in the median flow year but the effect on the amount exported to the Great Barrier Reef lagoon was even greater, the estuary showing a higher transmission efficiency in the high flow year. The total load in the low flow year was one-third less than that in the median flow year; however, the amount imported from the Great Barrier Reef lagoon was very similar since the behaviour of the system in the two scenarios was very similar over the long dry season.

Reference list

Baird, M. (2001) CSIRO *Simple estuarine response model: Technical description of the ecological model*. CSIRO Marine, PO Box 1538, Hobart, Tasmania 7001.

Baird, M.E. & Emsley, S.M. (1999) Towards a mechanistic model of plankton population dynamics. *Journal of Plankton Research* 21, 85ñ126.

Baird, M.E., Walker, S.J., Wallace, B.B., Webster, I.T. & Parslow, J.S. (2003) The use of mechanistic descriptions of algal growth and zooplankton grazing in an estuarine eutrophication model. *Estuarine, Coastal and Shelf Science* 56, 685ñ695.

Brooke, B., Bostock, H., Smith, J. & Ryan, D. (2006) *Geomorphology and sediments of the Fitzroy River coastal sedimentary system ñ Summary and overview.* Technical Report No. 47, CRC for Coastal Zone, Estuary and Waterway Management, Brisbane.

Douglas, G., Ford, P., Moss, A., Noble, B., Packett, B., Palmer, M., Revill, A., Robson, B., Tillman, P. & Webster, I. (2005) *Carbon and nutrient cycling in a subtropical estuary (the Fitzroy), Central Queensland*. Cooperative Research Centre for Coastal Zone, Estuary and Waterways Management.

Fennel, K., Spitz, Y.H., Letelier, R.M., Abbott, M.R. & Karl, D.M. (2001) Deep sea research, Part II. *Topical Studies in Oceanography* 49, 149ñ174.

Ford, P., Tillman, P., Robson, B. & Webster, I.T. (2005). Organic carbon deliveries and their flow related dynamics in the Fitzroy Estuary. *Marine Pollution Bulletin* 51, 119ñ127.

Furnas, M. (2003) *Catchments and corals. Terrestrial runoff to the Great Barrier Reef.* Australian Institute of Marine Science. Townsville.

Goto, N., Mitamura, O. & Terai, H. (2000) Seasonal variation in primary production of microphytobenthos at the Isshiki intertidal flat in Mikawa Bay. *Limnology* 1(2), 0133ñ0138.

Harris, G. P., Batley, G., Fox, D., Hall, D., Jernakoff, P., Molloy, R., Murray, A., Newell, B., Parslow, J., Skyring, G. & Walker, S. (1996) *Port Phillip Bay Environmental Study: Final Report*. Dickson, ACT, Australia, CSIRO.

Herzfeld, M., Andrewartha, J.R., Sakov, P. & Webster, I. (2006) *Numerical hydrodynamic modelling of the Fitzroy Estuary*. Technical Report No. 38, CRC for Coastal Zone, Estuary and Waterway Management, Brisbane.

Herzfeld, M., Waring, J. Parslow, J. Margvelashvili, N., Sakov P. & Andrewartha, J. (2005) *SHOC: Sparse hydrodynamic ocean code scientific manual*. CSIRO report, pp. 118.

Margvelashvili, N. (2003) *MECOSED: Model for estuarine and coastal sediment transport.* CSIRO report, pp. 53.

Margvelashvili, N., Herzfeld, M. & Webster, I. (2006) *Modelling of fine sediment transport in Fitzroy Estuary and Keppel Bay.* Technical Report No. 39, CRC for Coastal Zone, Estuary and Waterway Management, Brisbane.

Margvelashvili, N., Robson, B., Sakov, P., Webster, I.T., Parslow, J., Herzfeld, M. & Andrewartha, J. (2003) *Numerical modelling of hydrodynamics, sediment transport and biogeochemistry in the Fitzroy Estuary.* Cooperative Research Centre for Coastal Zone, Estuary and Waterway Management.

Mulholland, M.R. & Capone, D.G. (2000) *Trends in Plant Science* 5, 148ñ153.

Murray, A.G. & Parslow, J.S. (1999a) *Ecological Modelling* 119, 149ñ166.

Murray, A.G. & Parslow, J.S. (1999b) *Marine and Freshwater Research* 50, 597ñ611.

Murray, Alexander & Parslow, John. (1997) *Port Phillip Bay integrated model: Final report.* Canberra, CSIRO Division of Marine Research.

O'Neil, J.M., Metzler, P.M. & Glibert, P.M. (1997) *Oceanographic Literature Review* 44, 196.

Radke, L.C., Ford, P.F., Webster, I., Douglas, G., Oubelkheir, K., Atkinson, I., Robson, B., Verwey, P., MacKenzie, K. & Clementson, L. (2005) *Results of two dry-season surveys of Keppel Bay and Casuarina Creek: Biogeochemical properties of the water column and underlying sediments.* Geoscience Australia, Record 2005/18,121 pp.

Radke, L.C., Ford, P.W., Webster, I.T., Atkinson, I. & Oubelkheir, K. (2006) *Keppel Bay: Physical processes and biogeochemical functioning*. Technical Report No. 34, CRC for Coastal Zone, Estuary and Waterway Management, Brisbane.

Revill, A., Leeming, R. & Smith, C. (2006) Fitzroy River: *Intertidal mudflat biogeochemistry*. Technical Report No. 35, CRC for Coastal Zone, Estuary and Waterway Management, Brisbane.

Robson, B.J., Webster, I.T., Margvelashvili, N. & Herzfeld, N. (2006) *Scenario modelling: Simulating the downstream effects of changes in catchment land use.* Technical Report No. 41, CRC for Coastal Zone, Estuary and Waterway Management, Brisbane.

Soeteart, K., Middelburg, J.L., Herman, P.M.J., & Buis, K. (2000) *Earth Sciences Reviews* 51, 173ñ201.

Webster, I.T., Ford, P.W., Robson, B., Margvelashvili, N. & Parslow, J. (2003) *Conceptual models of the hydrodynamics, fine sediment dynamics, biogeochemistry and primary production in the Fitzroy Estuary.* Cooperative Research Centre for Coastal Zone, Estuary and Waterway Management.

Webster, I.T., Ford, P.W. & Tillman, P. (2005) *Marine Pollution Bulletin* 51, 165ñ173.

Wild-Allen, K., Herzfeld, M., Margvelashvili, N. & Rosebrock, U. (2006) *Fitzroy Estuary mudflat model.* Technical Report No. 36, CRC for Coastal Zone, Estuary and Waterway Management, Brisbane.

Appendix 1: Calibrated parameter values

Parameter	**Description**	**units**	**value**
ZL_E	Growth efficiency, large zooplankton	none	0.4
ZS_E	Growth efficiency, small zooplankton	none	0.4
SG_KN	Half-saturation of SG N uptake in SED	mg N m^{-3}	5.0
SG_KP	Half-saturation of SG P uptake in SED	mg N m^{-3}	5.0
PhyL_mL	Natural (linear) mortality rate, large phytoplankton (in sediment)	d^{-1}	0.2
PhyS_mL	Natural (linear) mortality rate, small phytoplankton (in sediment)	d^{-1}	0.2
MA_mL	Natural (linear) mortality rate, macroalgae	d^{-1}	0.01
SG_mL	Natural (linear) mortality rate, seagrass	d^{-1}	2.74×10^{-3}
MPB_mQ	Natural (quadratic) mortality rate, microphytobenthos	$d^{-1}(\text{mg N } m^{-3})^{-1}$	2×10^{-4}
ZL_mQ	Natural (quadratic) mortality rate, large zooplankton	$d^{-1}(\text{mg N } m^{-3})^{-1}$	3.5 x 10-4
ZS_mQ	Natural (quadratic) mortality rate, small zooplankton	$d^{-1}(\text{mg N } m^{-3})^{-1}$	1.5×10^{-2}
ZL_FDG	Fraction of growth inefficiency lost to detritus, large zooplankton	none	0.3
ZL_FDM	Fraction of mortality lost to detritus, large zooplankton	none	0.3
ZS_FDG	Fraction of growth inefficiency lost to detritus, small zooplankton	none	0.3
ZS_FDM	Fraction of mortality lost to detritus, small zooplankton	none	0.3
F_LD_RD	Fraction of labile detritus converted to refractory detritus	none	0.19
F_LD_DOM	Fraction of labile detritus converted to dissolved organic matter	none	0.7
NtoCHL	Nitrogen:chlorophyll *a* ratio in phytoplankton by weight	m^{-1}	7
k_w	Background light attenuation coefficient	none	0.15
k_DOR_N	DOR_N-specific light attenuation coefficient	$m^{-1}(\text{mg N } m^{-3})^{-1}$	2×10^{-3}
k_DetL	Detrital N-specific light attenuation coefficient	$m^{-1}(\text{mg N } m^{-3})^{-1}$	3.8×10^{-2}
k_TSS	TSS-specific light attenuation coefficient	$m^{-1}(\text{kg } m^{-3})^{-1}$	1000.0
k_C_fw	CDOM attenuation coefficient of fresh water	m^{-1}	5.4
k_SWR_PAR	fraction of incident solar radiation that is PAR	none	0.43
Q10	Temperature coefficient for rate parameters	none	2.0
PLumax	Maximum growth rate of PL at Tref	d^{-1}	1.8
PLrad	Radius of the large phytoplankton cells	m	1×10^{-5}
PLabsorb	Absorption coefficient of a PL cell	m^{-1}	10000
PLSh	Sherwood number for the PS dimensionless	none	1
PLn	Number of limiting nutrients	none	3
PSumax	Maximum growth rate of PS at Tref	d^{-1}	1.0
PSrad	Radius of the small phytoplankton cells	m	2.5×10^{-6}
PSabsorb	Absorption coefficient of a PS cell	m^{-1}	15000
PSSh	Sherwood number for the PL dimensionless	none	1
PSn	Number of limiting nutrients	none	3
MBumax	Maximum growth rate of MB at Tref	d^{-1}	0.45
MBrad	Radius of MPB cells	m	1×10^{-5}
MBabsorb	Absorption coefficient of a MPB cell	m^{-1}	70000
MBSh	Sherwood number for the PL dimensionless	none	1

Parameter	**Description**	**units**	**value**
MBn	Number of limiting nutrients	none	3
MAumax	Maximum growth rate of MA at Tref	d^{-1}	0.02
MAaA	Nitrogen specific absorption cross-section of MA	$m^2\ mgN^{-1}$	1×10^{-3}
MAn	Number of limiting nutrients	none	3
MAm	Stoichometry coefficient of phosphorus	none	2.4×10^{-6}
SGumax	Maximum growth rate of SG at Tref	d^{-1}	0.1
SGaA	Nitrogen specific absorption cross-section of SG	$m^2\ mgN^{-1}$	1×10^{-5}
SGm	Stoichometry coefficient of phosphorus	none	2.4×10^{-6}
ZSumax	Maximum growth rate of ZS at Tref	d^{-1}	3
ZSrad	Radius of the small zooplankton cells	m^{-1}	1.25×10^{-5}
ZSswim	Swimming velocity for small zooplankton	$m\ s^{-1}$	2×10^{-4}
ZLumax	Maximum growth rate of ZL at Tref	d^{-1}	0.15
ZLrad	Radius of the large zooplankton cells	m^{-1}	5×10^{-4}
ZLswim	Swimming velocity for large zooplankton	$m\ s^{-1}$	8×10^{-4}
TKEeps	TKE dissipation in water column	$m^2 s^{-3}$	1×10^{-6}
cf	Drag coefficient of the benthic surface	none	5×10^{-3}
Ub	Velocity at the top of the ben. bound. layer	$m\ s^{-1}$	0.1
ks	Sand-grain roughness of the benthos	m	0.1
F_RD_DOM	Fraction of refractory detritus that breaks down to DOM	none	0.8
r_floc	Rate at which TSS flocculates above 10 PSU	d^{-1}	1×10^{-2}
r_DetPL	Breakdown rate of labile detritus at 106:16:1	d^{-1}	5×10^{-2}
r_DetBL	Breakdown rate of labile detritus at 550:30:1	d^{-1}	5×10^{-2}
r_RD	Breakdown rate of refractory detritus	d^{-1}	4 x 10-5
r_DOM	Breakdown rate of dissolved organic matter	d^{-1}	1.76×10^{-3}
Tref	Reference temperature	^oC	20.0
Plank_resp	Respiration as a fraction of umax	none	3×10^{-2}
Benth_resp	Respiration as a fraction of umax	none	2.5×10^{-2}
NOumax	Maximum growth rate of *Trichodesmium* at Tref	d^{-1}	0.8
NOrad	Radius of *Trichodesmium* cells	m	2.5×10^{-6}
NOabsorb	Absorption coefficient of a *Trichodesmium* cell	m^{-1}	15000.0
NO_TG	Temperature below which growth of *Trichodesmium* cells slows down	^oC	24.75
NO_SG	Salinity above which growth of *Trichodesmium* cells slows down	none	45.0
NOSh	Sherwood number for *Trichodesmium*	none	1.0
NOn	Number of limiting nutrients for *Trichodesmium*	none	3
NO_mL	Linear mortality rate, *Trichodesmium*	d^{-1}	0.17
NO_mQ	Quadratic mortality rate for *Trichodesmium*	d^{-1}	5×10^{-2}
DFCtoNvar	Maximal to minimal C:N ratio in dinoflagellate	none	1.5
KO_aer	Oxygen half-saturation for aerobic respiration	$mg\ O\ m^{-3}$	500.0
r_nit_wc	Maximal nitrification rate in water column	d^{-1}	1×10^{-2}
r_nit_sed	Maximal nitrification rate in water sediment	d^{-1}	0.4
KO_nit	Oxygen half-saturation for nitrification	$mg\ O\ m^{-3}$	10000.0
Pads_r	Rate at which P reaches adsorbed/desorbed equilibrium	d^{-1}	1.0
Pads_Kwc	Freundlich Isothermic Const P adsorption to TSS in water column	$mg\ P\ kg\ TSS^{-1}$	200
Pads_Ksed	Freundlich Isothermic Const P adsorption to TSS in sediment	$mg\ P\ kg\ TSS^{-1}$	174.0
Pads_KO	Oxygen half-saturation for P adsorption	$mg\ O\ m^{-3}$	2000.0
Pads_exp	Exponent for Freundlich Isotherm	none	1.0

Parameter	**Description**	**units**	**value**
r_den	Maximum denitrification rate	d^{-1}	5.0
KO_den	Oxygen content at 50% denitrification rate	$mg\ O\ m^{-3}$	500.0
r_floc_sed	Rate of the TSS flocculation in sediment	d^{-1}	1×10^{-3}
r_bury_TSS	Rate of the TSS burying	d^{-1}	1×10^{-3}
r_immob_PIP	Rate of conversion of PIP to immobilised PIP	d^{-1}	1.2×10^{-3}
TR_TG	Temperature below which growth of *Trichodesmium* cells slows down	^{o}C	20
TRcrit	Wind stress below which *Trichodesmium* do well	Nm^{-2}	6.2×10^{-2}
TR_FDON	Proportion of fixed nitrogen immediately excreted as DOR_N	none	0.3
Fmax_Nit _sed	Maximum nitrification efficiency		1.0