Report on AIMS river nutrient data collected from downstream sites in major Queensland rivers draining to the Great Barrier Reef lagoon, 1987-2000.

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Description of sampling program

Streams draining to the GBR coast were generally sampled from bridges along the Bruce Highway. This highway was convenient for most rivers, far enough downstream to incorporate the bulk of the catchment area and its inputs, but far enough upstream to be within freshwater and out of the estuary, at least during wet-season flows. The principal objective of the sampling program was to determine nutrient loads carried by the major rivers adjacent to the Central-Southern sections of the GBR, for use in the compilation of a nutrient budget of the GBR shelf. River-nutrient data available at the time of this program's commencement (late 1980s) were poor and had mostly been collected during dry-season periods. THe Australian Institute of Marine Science (AIMS) persuaded local professional staff to sample on our behalf where possible (e.g. Bureau of Sugar Experiment Stations [BSES], Tully) or paid local personnel a small per-sample fee for collection. Considerable funding assistance was provided by the Great Barrier Reef Marine Park Authority (GBRMPA).

Six major rivers were sampled extensively, the Barron, South Johnstone, Tully, Herbert, Burdekin and Fitzroy. These rivers covered much of the Wet Tropics and the two main rivers of the Dry Tropics. Emphasis was given to wet-season sampling because of the crucial importance of this period to load calculations and because of the likely dynamic changes in nutrient concentrations during rainfall events. Collection personnel were asked to sample using a rainfall-mediated strategy, to sample sparsely until actual wet-season rainfall events, then to actively sample during these events, tapering off as the event concluded. Intensive sampling was then to be recommenced with the next rainfall event, though the whole wet season. This strategy worked better in some rivers than in others, the success largely dependent on the enthusiasm and commitment of the collection personnel. Clearly, rivers of the Wet Tropics, which have multiple wet-season discharge peaks, require greater sampling effort to capture these peaks than do rivers of the Dry Tropics, which typically only have one or two broad discharge peaks per year. A rank of these major data sets for their usefulness is given in Table 1.

The author regularly visited these collection personnel, refreshing supplies and returning to AIMS with the frozen water samples for analysis. During these collection trips, the author also took samples of convenience at the major rivers and also at rivers and creeks in between these. The latter streams included Alligator Creek, Haughton River and Barratta Creek to the south, and North Johnstone River, Russell River and Mulgrave River to the north. Unfortunately, sampling was quite intermittent in these small collections, so these small data sets are of much less value than the major data sets. They typically involve dry-season rather than wet-season sampling.

Table 1: Ranking success of river sampling program.

River	Rank (usefulness)	Reasons for success/failure
Tully	1	Regular monthly sampling plus rainfall-mediated additional sampling probably gave discipline to the program. The same team of sampling personnel carried program on for 13 years.
Burdekin	2	Program continued for around 12 years; A few changes of sampling personnel with slightly different priorities; considerable missing data.
S. Johnstone	3	Same team sampling, but for only 5 years, no TSS collected, but good program in other respects.
Fitzroy	3	Two teams collecting samples, good wet-season sampling, but only for 6 years, unfortunately, no TSS until 1992.
Herbert	4	Sampling continued for 10 years, but less disciplined in terms of wet-season sampling; much missing data near end of program.
Barron	5	Relatively poor discipline for wet-season sampling, relatively intermittent sampling, a number of sample collectors and much missing data.

Excluded data sets

Further nutrient sampling was made at various catchment and upstream sites of the Herbert and Tully River basins, but these are not included in this coastal data set. Additional nutrient sampling was made by other AIMS personnel in a number of rivers along the Cape York peninsula, but these samples were quite patchy, mainly dry-season and taken in the estuaries. They are not included in this set. Some limited sampling was conducted by National Park personnel in the Normanby River for Dr. Miles Furnas of AIMS. He should be directly contacted for access to these samples.

Replication of water samples

All water samples were collected with a clean bucket and rope from the bridges near the centre of flow in each stream. Single or duplicate water samples were collected (Sample Replicates) and all were sub-sampled in duplicate for analysis (Analytical Replicates). The whole dataset with all replicates are provided in 'AIMS dataset 1.xls'. Each nutrient value in

'AIMS dataset 2' is the mean of either two or four measurements. Access to the data sets compiled in these Excel sheets for research purposes can be obtained on request to ACTFR (Jon Brodie) or AIMS (Miles Furnas).

Processing of water samples

The local collection personnel processed the samples at their laboratory or at their private homes, usually within an hour or so of collection. The author processed samples either on site using a battery-operated vacuum pump or at home, within 4 hours of collection. All water samples for dissolved nutrient analysis other than silicate (NO_2, NO_3, NH_4, PO_4, DON, DOP) were pre-filtered by plastic syringe through pre-rinsed, 25 mm diameter, Whatman GF/F filters (nominal porosity 0.7 μm) into 10-mL Sarstedt polypropylene vials and immediately frozen for later analysis. Separate, filtered samples for silicate were kept unfrozen following the discovery of polymerisation problems when defrosted. Water samples for particulate fractions (PN and PP) were separately filtered onto pre-combusted, 25 mm diameter, Whatman GF/F filters, which were folded over in half to retain the particulate matter, wrapped in foil and immediately frozen for later analysis (see following comment in the analyses paragraph below on differences to more conventional method). For TSS analyses, variable volumes of water samples, depending on the turbidity, were filtered through 47 mm diameter, pre-weighed, Sartorius membrane filters (0.4 μm porosity), and stored in small vials or petri dishes for later weighing.

Contamination of some dissolved nutrient samples was suspected in the early years of sampling at Tully, observed as relatively high concentrations of ammonia and orthophosphate. This possible contamination was traced to a commonly-used freezer at BSES, Tully, which was used for the water samples as well as for storing soil samples that had an obvious fertilizer odour. A new freezer was purchased for BSES to store only samples from the water sampling program (see note in Mitchell *et al.*, 2007). Collection personnel for other rivers were asked to use clean freezers where possible.

Analyses of water samples

Chemical analyses of these water samples were made periodically at the AIMS laboratory. All dissolved nutrient analyses were determined by segmented-flow autoanalysis, with samples for Total Dissolved nutrients (TDN, TDP) previously treated using 12-h ultraviolet (UV) oxidation. DON and DOP were determined by subtraction of DIN and DIP concentrations respectively. This UV oxidation technique, developed by AIMS for very low-level oceanic samples, may have resulted in a slight underestimate of DON and DOP for river samples compared to the more traditional techniques of alkaline persulfate or Kjeldahl digestion. The PN and PP samples were digested with persulfate before analysis. The author considers that the separate measurement of these particulate fractions is more complete than the more traditional method of treating unfiltered samples and calculating PN and PP by difference from filtered samples. Hence, the AIMS values for both DON, DOP may be slight under-estimates, while the PN, PP values may be slight over-estimates, compared to other laboratories. The method used for determinations of DIN, DIP and TSS are the traditional methods, so these values should be comparable with those from other laboratories. Indeed, various low-level nutrient trials and inter-calibrations over the sampling period have borne this out.

Strategic error in water sampling program

Samples for suspended sediment (TSS) were only routinely collected from around 1992-93, after it was realised how useful this measurement would be. Unfortunately, the data sets for the Fitzroy and South Johnstone are largely devoid of these measurements.

Missing data

Unfortunately, there are many missing values in the complete data set. In some cases, only some nutrients were processed, while in other cases samples went missing from the analytical section at AIMS, or were accidentally analysed twice for the same nutrient forms, effectively preventing completion of the whole nutrient suite. In some of the intermittently sampled rivers, missing samples denoted periods in which other samples were given priority and these samples mistakenly discarded.

Data summary

Sampling site locations for the rivers and creeks in the AIMS dataset files, with brief comments on the timing and value of data collected for each stream are listed in Table 2. These locations are also shown on the attached Google-Earth map "AIMS river sampling locations.kmz".

Data analysis

Parts of this data set have been previously analysed, interpreted and published in journal articles, conference papers, book chapters and books. A selection of these publications include:

Furnas, M.J. 2003. Catchments and Corals: Terrestrial Runoff to the Great Barrier Reef. Australian Institute of Marine Science and Reef CRC, Townsville.

Mitchell, A., Reghenzani, J., Faithful, J.W., Furnas, M. & Brodie, J.E. 2009. Relationships between land use and nutrient concentrations in streams draining a ‘wet-tropics’ catchment in northern Australia. *Marine and Freshwater Research*, 60:1097-1108.

Mitchell, A., Reghenzani, J. and Furnas, M. 2001. Nitrogen levels in the Tully River – a long-term view. Water Science and Technology, 43: 99–105

Mitchell, A., Reghenzani, J., Furnas, M., Brodie, J. and Lewis, S. 2006. Nutrients and suspended sediments in the Tully River: Spatial and temporal trends. ACTFR Report. No. 06/10 for FNQNRM Tully CCI. ACTFR, James Cook University, Townsville, 115 pp.

Mitchell, A., Lewis, S., Brodie, J., Bainbridge, Z. and Maughan, M. 2007a. Water quality issues in the Burdekin Region. ACTFR Report 07/03 for the BDTNRM CCI. ACTFR, JCU, Townsville, 60 pp.

Furnas, M. and Mitchell, A. 2001. Runoff of terrestrial sediment and nutrients into the Great Barrier Reef World Heritage Area. In: E. Wolanski (Ed.) Oceanographic Processes of Coral reefs: Physical and Biological Links in the Great Barrier Reef. CRC Press, Boca Raton. pp 37-51.

Mitchell, A. 1988. River inputs of nutrients. In: C.L.Baldwin (Ed.), *Workshop on nutrients in the Great Barrier Reef region*, 16-22. Workshop Series No. 10, Great Barrier Reef Marine Park Authority, Townsville.

Mitchell, A.W. and Furnas, M.J. 1994. River inputs of N and P to the Central Great Barrier Reef. *Proceedings of the Australian Society of Sugar Cane Technologists* 16: 147-153.

Mitchell, A.W. and Furnas, M.J. 1997. Terrestrial inputs of nutrients and suspended sediments to the Great Barrier Reef lagoon. In: Turia, N. and Dalliston, C. (Eds.). The Great Barrier Reef: science, use and management. Great Barrier Reef Marine Park Authority, Townsville, Australia.

Mitchell, A.W. and Furnas, M.J. 2001. River loggers - a new tool to monitor riverine suspended particle fluxes. *Water Science and Technology* 43(9): 115-120.

Mitchell, A., Rasmussen, C., Blake, S., Congdon, R., Reghenzani, J., Saffigna, P. and Sturmey, H. 1991. Nutrient status and trends in waters of the Great Barrier Reef Marine Park. In: Yellowlees, D. (Ed.) *Land use patterns and nutrient loading of the Great Barrier Reef Region*. Sir George Fisher Centre for Tropical Marine Studies, James Cook University, Townsville. pp. 108-161.

Mitchell, A.W., Reghenzani, J., Hunter, H.M. & Bramley, R.G.V. 1996. Water quality and nutrient fluxes from river systems draining to the Great Barrier Reef. In: Eyles et al (Eds.) Proceedings of the Conference on the Downstream Effects of Land Use, April, 1995, Central Queensland University, Rockhampton.

Mitchell, A.W., Bramley, R.G.V., and Johnson, A.K.L. 1997, Export of nutrients and suspended sediment during a cyclone-mediated flood event in the Herbert River catchment, Australia. *Marine and Freshwater Research* 48, 79-88.

Table 2: Sampling site locations for each river and creek with comments on the sample timing and value.

River/Creek	Location	Latitude	Longitude	Comment
Alligator Ck	Bruce H'way	19^{o} 23' 19.97"S	146^{o} 57' 25.77"E	Intermittent, short set
Barratta Ck	Clare			QWRC site, long early set
Barratta Ck	Bruce H'way	19^{o} 34' 7.66"S	147^{o} 12' 42.42"E	Intermittent, short recent set
Barron R	Bruce H'way	16^{o} 52' 8.16"S	145^{o} 44' 10.07"E	Small intermittent data set, at estuarine location
Barron R	Kamerunga	16^{o} 52' 24.55"S	145^{o} 44' 8.98"E	Major data set, but much interrupted, many missing values
Burdekin R	Bruce H'way	19^{o} 38' 21.97"S	147^{o} 22' 40.41"E	Major data set with long sampling history
Burdekin R	Clare			QWRC site, long early set
Fitzroy R	Barrage	23^{o} 21' 37.42"S	150^{o} 29' 52.09"E	Major data set but only over 4-yr period
Fitzroy R	RCC site			Slight upstream site from Barrage, only 1996 wet season
Haughton R	Bruce H'way	19^{o} 33' 22.99"S	147^{o} 6' 19.98"E	Intermittent, short set
Herbert R	Gairlock	18^{o} 36' 58.14"S	146^{o} 11' 4.79"E	Intermittent, short set, downstream from John Rowe Bridge
Herbert R	Bruce H'way	18^{o} 37' 46.23"S	146^{o} 9' 54.19"E	Major data set, though somewhat intermittent, John Rowe Bridge
Mulgrave R	Lower	17^{o} 20' 56.79"S	145^{o} 55' 33.88"E	Intermittent, shorter set
Mulgrave R	Bruce H'way	17^{o} 21' 50.99"S	145^{o} 54' 55.25"E	Intermittent
Murray R	Bruce H'way	18^{o} 1' 45.66"S	145^{o} 55' 28.81"E	Intermittent
N. Johnstone R	Bruce H'way	17^{o} 30' 22.11"S	145^{o} 59' 34.09"E	Intermittent
Ross R	Nathan Bridge	19^{o} 18' 29.07"S	146^{o} 45' 40.62"E	Intermittent, many missing data
Russell R	Boulders			3 samples only by Sheridan Morris
Russell R	Cane			3 samples only by Sheridan Morris - kept here to show high nitrate in a cane drain
Russell R	Bruce H'way	17^{o} 25' 27.77"S	145^{o} 54' 39.76"E	Intermittent
Russell R	Lower	17^{o} 23' 40.80"S	145^{o} 57' 16.57"E	Intermittent, shorter set
S. Johnstone R	Bridge	17^{o} 35' 56.60"S	145^{o} 59' 54.09"E	Major data set, good wet-season sampling
Tully R	Bruce H'way	17^{o} 59' 33.25"S	145^{o} 56' 32.96"E	Major (best) data set, good wet-season sampling