CSIRO PUBLISHING
www.publish.csiro.au/journals/mfr *Marine and Freshwater Research*, 2009, **60**, 1081–1090

Identifying the land-based sources of suspended sediments, nutrients and pesticides discharged to the Great Barrier Reef from the Tully–Murray Basin, Queensland, Australia

Zoe T. Bainbridge[A,D], *Jon E. Brodie*[A], *John W. Faithful*[A,C], *Damon A. Sydes*[B] *and Stephen E. Lewis*[A]

[A]Australian Centre for Tropical Freshwater Research, James Cook University, Townsville, Qld 4811, Australia.
[B]Cassowary Coast Regional Council, Tully, Qld 4854, Australia.
[C]Present address: Golder Associates, Calgary, AB T2P 3T1, Canada.
[D]Corresponding author. Email: zoe.bainbridge@jcu.edu.au

Abstract. To assist in the development of the Tully Water Quality Improvement Plan, a subcatchment water quality monitoring program was undertaken to identify the pollutants of concern and their land-based sources. Monitoring of suspended sediments, nutrients and pesticides in subcatchment waterways was conducted during the 2005–06 and 2006–07 wet seasons, which both had above average annual flows. We found distinct water quality signals from the basin's major land uses (forest, grazing, urban, sugarcane and banana cultivation), except for suspended sediment concentrations, which were low across all land uses when compared with neighbouring river catchments. This reflects the high ground cover of the basin and the location of intensive agriculture on low sloping areas of the floodplain, minimising the potential for erosion. Nitrate concentrations were elevated in streams draining sugarcane, indicating fertiliser export from intensive agricultural landscapes. Residues of the herbicides diuron and atrazine were detected at sites draining sugarcane, and on occasion exceeded national ecological protection trigger values, which highlights a potential threat to downstream wetlands of recognised national significance. Herbicides were also detectable offshore in flood plumes of the Tully–Murray Rivers, with some concentrations of diuron above lowest observable effect concentrations for specific species of seagrass and corals. Run-off of nitrate and diuron were identified as key water quality issues in the Tully–Murray basin.

Additional keywords: agricultural runoff, diuron, floodplume herbicides, nitrate, water quality.

Introduction

The increasing run-off of terrestrial materials to the marine environment is a major stressor of coral reefs (e.g. Wilkinson 2004). While the Great Barrier Reef (GBR) of Australia is one of the best managed and protected marine systems, negative effects of agricultural run-off to GBR coral reefs have been reported (e.g. Fabricius *et al*. 2005; DeVantier *et al*. 2006). In 2003, the Australian and Queensland Governments established the Reef Water Quality Protection Plan ('Reef Plan'; Anonymous 2003) to reduce the run-off of sediments, nutrients and pesticides into the GBR lagoon (Hutchings *et al*. 2005; Haynes *et al*. 2007). This objective is achieved through the development of regional Water Quality Improvement Plans (WQIP) across the GBR catchment area (see Kroon 2009).

The Tully–Murray basin (2800 km^2) is situated in the Wet Tropics of north Queensland and forms one of the WQIP regions (Fig. 1*a*; see also fig. 1 in Kroon 2009). In the last two–three decades, the Tully–Murray coastal floodplain has undergone extensive modification largely due to the expansion of the sugarcane and horticulture (banana and pawpaw) industries (Mitchell *et al*. 2006). Tourism forms another key industry within the region; the township of Mission Beach is the access point to the nearby islands and their associated fringing reefs (e.g. Dunk and Bedarra Islands). These reefs, as well as other inshore coral reefs of the Wet Tropics region, are degraded due to poor water quality (and other stressors), which has been linked to the run-off of terrestrial materials from agricultural lands (Fabricius *et al*. 2005; DeVantier *et al*. 2006; Brodie *et al*. 2007; Wolanski *et al*. 2008).

Dissolved inorganic nitrogen run-off associated with nitrogen fertiliser loss has been identified as a major water quality issue in the Tully–Murray basin (Mitchell *et al*. 2001, 2006). Additionally, diuron residues have been detected in marine sediments immediately adjacent to the basin (Haynes *et al*. 2000*a*). Similar studies in other catchments of the GBR (e.g. Bramley and Roth 2002; Mitchell *et al*. 2005; Hunter and Walton 2008; Rohde *et al*. 2008; Davis *et al*. in press) have also demonstrated that suspended sediment, nutrient and pesticide concentrations are elevated in subcatchment waterways draining intensive agriculture, compared with catchments under natural vegetation, such as the rainforest headwater streams of the Wet Tropics region and those draining into Princess Charlotte Bay, Cape York. High seasonal river flows transport these terrestrial pollutants to the adjacent marine environment in freshwater plumes where

10.1071/MF08333 1323-1650/09/111081

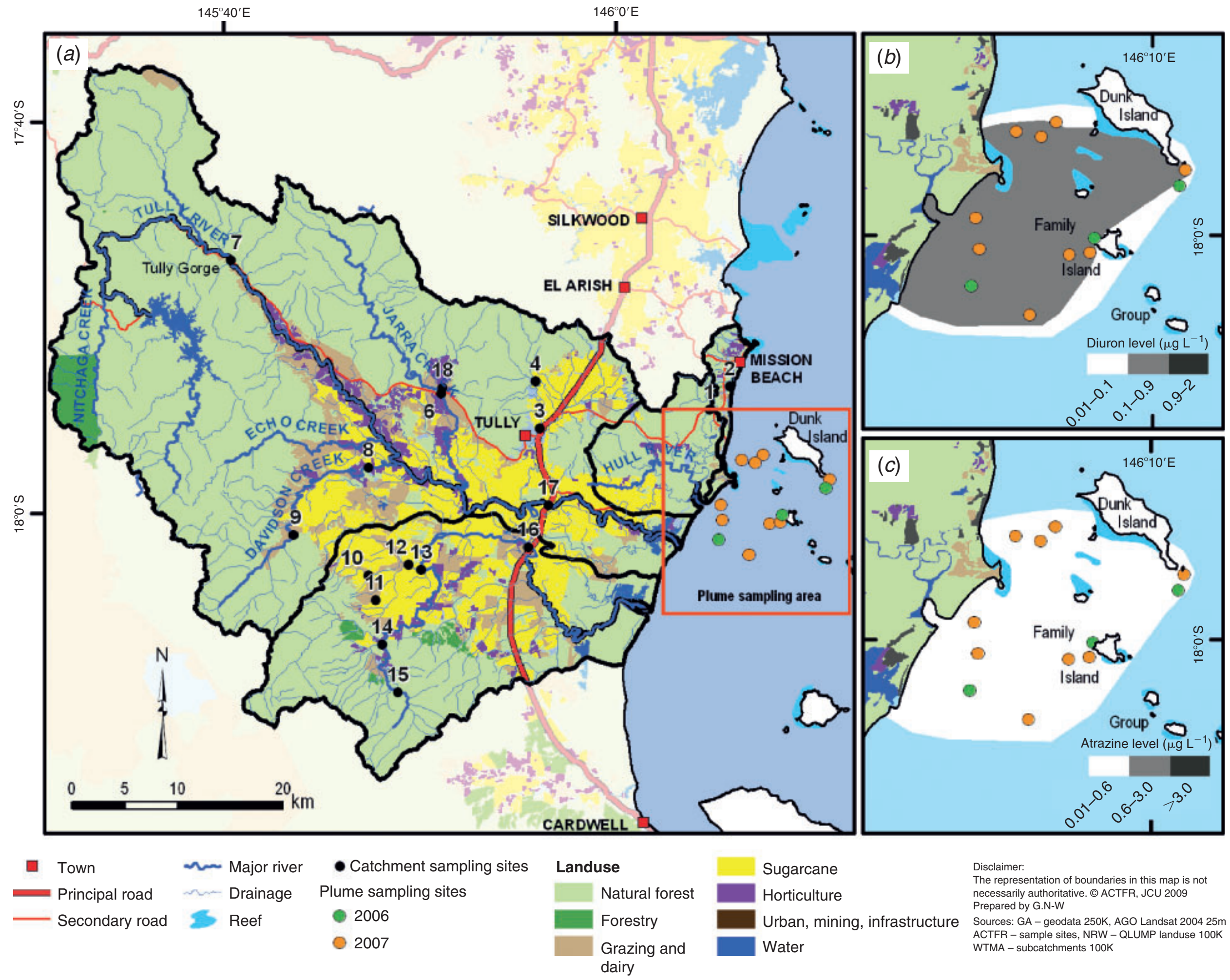

Fig. 1. (*a*) Land-use map of the Tully–Murray basin illustrating subcatchment and river water plume sampling sites. (*b*) Diuron residue concentrations in the plume are depicted by contour maps that show herbicide residues can travel considerable distances in the marine environment at biologically significant levels. The contour map intervals are based on the analytical level of detection (0.01 $\mu g\,L^{-1}$), the lowest observable effect concentration on marine plants (0.1 $\mu g\,L^{-1}$; Haynes *et al*. 2000*b*) and the current GBR water quality trigger value (0.9 $\mu g\,L^{-1}$; GBRMPA 2009), using the maximum concentration measured furthest offshore irrespective of year. (*c*) Atrazine residue concentrations in the plume are also shown. Atrazine contour map intervals are based on the analytical level of detection (0.01 $\mu g\,L^{-1}$), the locally derived GBR water quality trigger value (0.6 $\mu g\,L^{-1}$; GBRMPA 2009) and the current lowest observable effect concentration on marine plants (3 $\mu g\,L^{-1}$; Jones and Kerswell 2003).

they impinge on mangrove, seagrass and coral reef communities (Devlin and Brodie 2005; Devlin and Schaffelke 2009).

In this paper, we identify pollutant sources and characterise the water quality signals of the different land uses within the Tully–Murray basin. Our subcatchment monitoring program specifically investigated the run-off of suspended sediments (SS), nutrients and pesticides during wet season (November–April) flood events that coincide with the transport of the bulk of these materials (Mitchell *et al*. 1997, 2005; Furnas 2003). The Tully–Murray River freshwater plumes generated by the wet season flood events were also sampled for pesticide residues to provide a preliminary assessment of risk to the key marine ecosystems (e.g. seagrass, coral reefs) adjacent to the catchment (Fig. 1*a*). Specifically, the objectives of this study were to: (1) identify sources of sediments, nutrients and pesticides from specific land uses within subcatchments of the Tully–Murray basin; (2) measure concentrations of pesticide residues in the plumes resulting from major flow events in the Tully–Murray Rivers and assess the significance of these concentrations to marine ecosystem health; (3) provide high-quality input data to parameterise and validate catchment modelling (see Armour *et al*. 2009); and (4) assist in the identification of key water quality issues in the Tully–Murray basin for the WQIP process.

Materials and methods

Site selection within the study area

Subcatchment waterway sites were selected to represent the major land uses of the region, and were classed as sugarcane, grazing, urban, banana, or natural forest land use categories, as defined using Queensland Land Use Mapping Program data (Table 1; see Faithful *et al*. 2008). Sites were also selected based on wet season access to the site and the size of the waterway. A total of 16 sites were selected for the monitoring program, including 11 subcatchments of the Tully–Murray basin, as well as a transect of locations along both the Tully and Murray Rivers (Fig. 1).

It was expected that concentrations of SS, nutrients and pesticides measured at each subcatchment site would reflect the dominant land use of that subcatchment, as each land use utilises very different management regimes. For example, land uses such as sugarcane and horticulture use considerable rates of fertilisers and pesticides, and we thus expect to measure significant concentrations of nitrogen, phosphorus and certain pesticide residues in water draining these land uses. We also expect to see a change in the proportion of nutrient species draining these types of intensive land uses, such as a shift from the leakage of natural nutrient forms (e.g. dissolved organic nitrogen) to a dominance of dissolved inorganic nitrogen (e.g. nitrate) in fertilised cropping conditions (Brodie and Mitchell 2005).

Sampling

Over the monitoring period, considerable rainfall occurred across the Tully–Murray basin with ~3 622 000 ML and ~3 977 000 ML of discharge measured by the Tully River gauge at Euramo (Queensland Natural Resources and Water flow gauge 113006A) in the 2005–06 and 2006–07 water years respectively. These were ranked the ninth and eighth largest annual discharge volumes, respectively, on the 35-year gauge record. We note that flow discharge over these two wet seasons may have been higher due to overbank flows (see Wallace *et al*. 2009). Approximately 60% of the annual flow in both of these water years occurred during the wet season months January to April. During the first wet season, sampling was conducted during two small 'first flush' events in mid and late January 2006 to capture initial high concentration pollutant run-off from the immediate catchment area, as well as during the larger, catchment-wide flow events of late March–early April 2006 that were largely generated by Tropical Cyclone Larry. The sampling regime in the 2006–07 wet season was limited due to funding constraints, with sampling efforts focussed on the large flow events that occurred in late January–early February and March 2007. Refer to Faithful *et al*. (2008) for additional climate and flow data for the two monitored wet seasons.

Over the 2005–06 and 2006–07 wet seasons, 192 water samples were collected for the analyses of SS and nitrogen and phosphorus species. Ninety-two water samples were also collected for the analysis of pesticide residues. Surface water samples (top 50 cm of water column) were collected following significant rainfall events that triggered stream flow. Where possible, a stratified sampling approach to collect samples over the rising, peak and falling stages of the flow hydrograph was conducted. Water samples were collected in pre-rinsed 1-L polypropylene bottles using an extendable sampling pole for total suspended solids (suspended sediments), unfiltered nutrient samples were subsampled into 60-mL polypropylene vials (Sarstedt, Germany), with filterable nutrients filtered on-site through pre-rinsed filter modules (MiniSart 0.45 μm cellulose acetate, Sartorius, Germany) into six 10-mL polypropylene vials (Sarstedt, Australia). Nutrient samples were immediately placed on ice and frozen within 12 h of sampling. Pesticide samples were collected in 1-L solvent-washed amber glass bottles prepared by the Queensland Health and Forensic Scientific Services (QHFSS) laboratory. Where it was not possible to collect samples using the pole, samples were collected in a bucket that was rinsed with site water before sample collection. Samples were collected from the centre of the channel flow where possible and every effort was made to ensure samples were collected from the main flow, away from the backwash at the riverbank.

Surface water samples were also collected from the freshwater plumes generated by the Tully–Murray Rivers for pesticide residue analyses. Sample trips were timed to coincide with peak river discharge events on 4 April 2006 and 2 February 2007. Four and nine samples, respectively, were collected in the coastal GBR lagoon along a transect between the mouth of the Tully River and Dunk Island (Fig. 1*a*). The river water plume samples were collected with a bucket and rope from a research vessel and subsampled into 1-L solvent-washed amber glass bottles (supplied by QHFSS) and refrigerated.

Laboratory analyses

Water samples were analysed at the Australian Centre for Tropical Freshwater Research Laboratory, James Cook University for SS, total nitrogen (TN), total phosphorus (TP), total filterable nitrogen (TFN) and total filterable phosphorus (TFP), ammonia, oxidised nitrogen (NO_x-N: nitrate + nitrite) and filterable reactive phosphorus (FRP). Samples for SS analyses were filtered through pre-weighed Whatman (England) GF/C filter membranes (nominally 1.2 μm pore size) and oven-dried at 103–105°C for 24 h and reweighed to determine the dry SS weight as described in APHA (2005). Samples for TN, TP, TFN and TFP were digested in an autoclave using an alkaline persulfate technique (modified from Hosomi and Sudo 1986) and the resulting solution simultaneously analysed for NO_x-N and FRP by segmented flow auto-analysis using an ALPKEM (Texas, USA) Flow Solution II. The analyses of NO_x-N, ammonia and FRP were also conducted using segmented flow auto-analysis techniques following standard methods (APHA 2005). Particulate nutrient concentrations were estimated by the subtraction of the total filterable nutrient concentrations from the total nutrient concentrations. Similarly, dissolved (filterable) organic nitrogen (DON) and phosphorus (DOP) were estimated by the subtraction of NO_x-N and ammonia (for nitrogen) and FRP (for phosphorus) from the TFN and TFP concentrations.

The water samples collected for pesticide analyses were analysed by liquid chromatography mass spectrometry (LCMS) and gas chromatography mass spectrometry (GCMS) at the National Association of Testing Authorities accredited QHFSS Laboratory. The extraction procedures and analytical methods for organochlorine, organophosphorus and synthetic pyrethroid pesticides, urea and triazine herbicides are described in Lewis *et al*. (2009). A total of 122 pesticides were analysed, with detection limits ranging from 0.01 to 1 $\mu g\,L^{-1}$ (see Table A1, available as an Accessory Publication on the web).

Table 1. Sample site land use and upstream catchment area details

Grey shaded land uses indicate dominant land use. Areas of light grey shade represent other land uses that consist of >10% of the subcatchment area

Land-use category	Site ID	Site name	Upstream catchment area (km^2)	Forest		Sugarcane		Horticulture		Grazing		Urban	
				(%)	(km^2)	(%)	(km^2)	(%)	(km^2)	(%)	(km^2)	(%)	(km^2)
Forest	4	Bulgun Creek	32.1	99	32	0.6	0.2	0.0	0.0	0.0	0.0	0.3	0.1
	9	Davidson Creek (Fishtail)	93.3	98	91	0.0	0.0	0.0	0.0	2.4	2.2	0.0	0.0
	15	Murray River (Murray Falls)	39.1	100	39	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	14	Murray River (Jumbun)	62.8	97	61	0.3	0.2	1.8	1.1	0.4	0.2	0.2	0.1
	1	North Hull River	12.9	100	12.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	7	Tully Gorge	505	93	471	0.0	0.0	0.0	0.0	6.7	34	0.0	0.0
	6	Jarra Creek[A]	181	96	174	0.1	0.1	2.5	4.5	1.3	2.4	0.0	0.0
Sugarcane	3	Banyan Creek (Highway)	81.3	49	40	41	34	1.3	1.1	5.1	4.1	3.3	2.6
	12	Kyambul (K1)	56.3	18.7	10.5	60	34	0.4	0.2	20	12	0.1	0.0
	13	Kyambul (Copperhead Road)	57.3	18.6	10.6	60	35	0.4	0.2	20	12	0.1	0.0
	16	Murray River (Highway)	291	60	175	28	80	3.9	11.4	8.1	24	0.2	0.5
	10	Warrami Ck (Blackman Road)	6.5	44	2.9	37	2.4	0.0	0.0	19	1.2	0.0	0.0
	17	Tully River (Euramo)	1395	77	1076	9.8	136	3.3	46	5.9	82	0.7	9.8
Banana	18	Marquette Creek	31	94	30	0.0	0.0	4.6	1.45	1.3	0.4	0.05	0.01
Grazing	11	Campbell's Creek	1.6	28	0.4	0.0	0.0	0.0	0.0	72	1.1	0.0	0.0
Urban	2	Porters Creek	1.0	35	0.4	0.0	0.0	1.0	0.01	27	0.3	37	0.4

[A]9% of the Jarra Creek subcatchment is designated as Defence area, which has been incorporated into Forest.

Results

Catchment land-use water quality characteristics

Individual subcatchment sites have been grouped within each of the five land-use categories and compared across the two monitored wet seasons for the water quality parameters SS, nitrogen and phosphorus species and the herbicides atrazine and diuron (Fig. 2*a–h*; Table A2, available as an Accessory Publication on the web).

SS concentrations were uniformly low across all land uses of the Tully–Murray basin, with median concentrations $\leq$25 mg L^{-1}, except for the urban land use (65 mg L^{-1}) in the 2006–07 wet season (Fig. 2*a*). The lowest SS concentrations were associated with the forest and grazing land-use categories. Some samples collected on the rising stage of flow events in both wet seasons fell into the extreme outlier range, particularly for the sugarcane land-use category with a peak of 520 mg L^{-1} at the Warrami Creek site (Fig. 2*a*).

NO_x-N concentrations were elevated in the sugarcane, banana and urban land-use categories compared with the forest land use (Fig. 2*b*). The two Kyambul sites, which have the largest percentage of the sugarcane land use in their upstream catchment areas (>60%), were only monitored in the first wet season. As a result, the median NO_x-N concentration for this category was higher in the 2005–06 wet season compared with the 2006–07 wet season (i.e. 720 μg L^{-1} compared with 460 μg L^{-1}) (Fig. 2*b*). NO_x-N concentrations for the grazing land use were lower than the intensive land uses of the region, with TN dominated by other species, namely DON (Figs 2*b*, 3).

Median concentrations of PN, PP and DON were all consistently higher in the sugarcane, grazing and urban land uses compared with the forest land use (Fig. 2*c–e*). FRP concentrations were very low across all land uses (median $\leq$10 μg L^{-1}), except the grazing land-use site (median FRP concentration of 33 μg L^{-1}) (Fig. 2*f*). Elevated ammonia concentrations were also detected at the urban site (Fig. 3).

Residues of several herbicides were detected in the Tully–Murray subcatchment waterways, including ametryn, atrazine (and its degradation products desethyl and desisopropyl atrazine), diuron, hexazinone and simazine (Table A2*b*). The herbicides atrazine (and degradation product desethyl atrazine), diuron and hexazinone were detected frequently in the sugarcane land use, with peak concentrations of 1 μg L^{-1}, 19 μg L^{-1} and 3.6 μg L^{-1} respectively (Fig. 2*g*, *h*, Table A2*b*). Pesticide residues (of those analysed; see Table A1) were not detected in the forest, banana, urban, or grazing land-use categories, except for one low level detection of diuron (0.02 μg L^{-1}) at Davidson Creek (forest land use) during peak flow conditions in the 2005–06 wet season (Fig. 2*g*, *h*). While this site appears not to drain sugarcane (see Table 1), the sampling location is immediately proximal to sugarcane paddocks that may have influenced this particular sample.

Atrazine residues exceeded the ANZECC and ARMCANZ (2000) ecological protection trigger value (99% species protection) of 0.7 μg L^{-1} in 3 of the 32 samples where atrazine was detected over the two wet seasons (Fig. 2*g*). The ANZECC and ARMCANZ (2000) ecological protection trigger value (low reliability guideline) of 0.2 μg L^{-1} for diuron was also exceeded in 23 of the 36 samples where diuron was detected (Fig. 2*h*). Although hexazinone residues were commonly detected, concentrations were well below the ecological protection trigger value (low reliability guideline) of 75 μg L^{-1} (Table A2*b*). Ametryn, desisopropyl atrazine and simazine were detected less frequently at concentrations just above the level of analytical detection (0.01 μg L^{-1}). While the ANZECC and ARMCANZ (2000) ecological protection trigger values are specifically designed for low flow conditions, they are the only available reference to assess the risk of pesticide residues in the freshwater environment.

Herbicide residues in the Tully–Murray River water plumes

Three herbicide residues were detected in both wet season river flood plumes, including atrazine (and its degradation product desethyl atrazine), diuron and hexazinone (Table A3, available as an Accessory Publication on the web). While these herbicides detected in the plume did not exceed the locally derived ecological protection trigger values for the GBR lagoon (GBRMPA 2009), 7 of the total 13 samples collected exceeded the current lowest observable effect concentration (LOEC) for diuron (0.1 μg L^{-1} for seagrass species *Halophila ovalis* and *Zostera capricorni*; Haynes *et al*. 2000*b*), which were detected at least 15 km from the river mouth (Fig. 1*b*). Atrazine residues were also detected in the plume to the extent of Dunk Island and the Family Island Group (Fig. 1*c*).

Discussion

The above average annual flows in the Tully–Murray basin during the 2005–06 and 2006–07 wet seasons allowed for an assessment of the potential exposure of land-based pollutants to downstream freshwater and marine receiving water bodies during large flow events. Specifically, the catchment to marine monitoring program was able to identify discernable differences in water quality parameters, particularly for nitrogen species and herbicides from specific land uses within the study basin, and to assess the risk of herbicide residues to adjacent marine ecosystems.

Catchment land-use water quality characteristics

Identifying sites to represent the banana and urban land-use categories was difficult in this study as natural forest (77%), sugarcane cultivation (10%) and grazing (6%) land uses dominate the Tully River catchment area. Similar proportions of land use also occur in the Murray River catchment (Table 1). The forest land use is generally confined to the upland rim of most of the basin's subcatchments, with agriculture, grazing and urban land uses located on the lowland floodplain in much smaller proportions (Fig. 1*a*). As a result, a single land use cannot easily be represented in isolation from other land-use influences, and the water quality signal from a particular land use of interest may be diluted by the subcatchments' major land use (e.g. forest or sugarcane). For example, Marquette Creek, which was chosen to represent the banana land-use category, only contains 4.6% banana in the small upstream catchment area (31 km^2), with the remainder of the catchment consisting primarily of natural forest. The median NO_x-N concentration for this site was only slightly elevated over that of the forest land-use category, suggesting that the water quality influence of bananas has been diluted.

Catchment disturbances have resulted in only minor increases in sediment loss in the Tully–Murray basin, with median SS

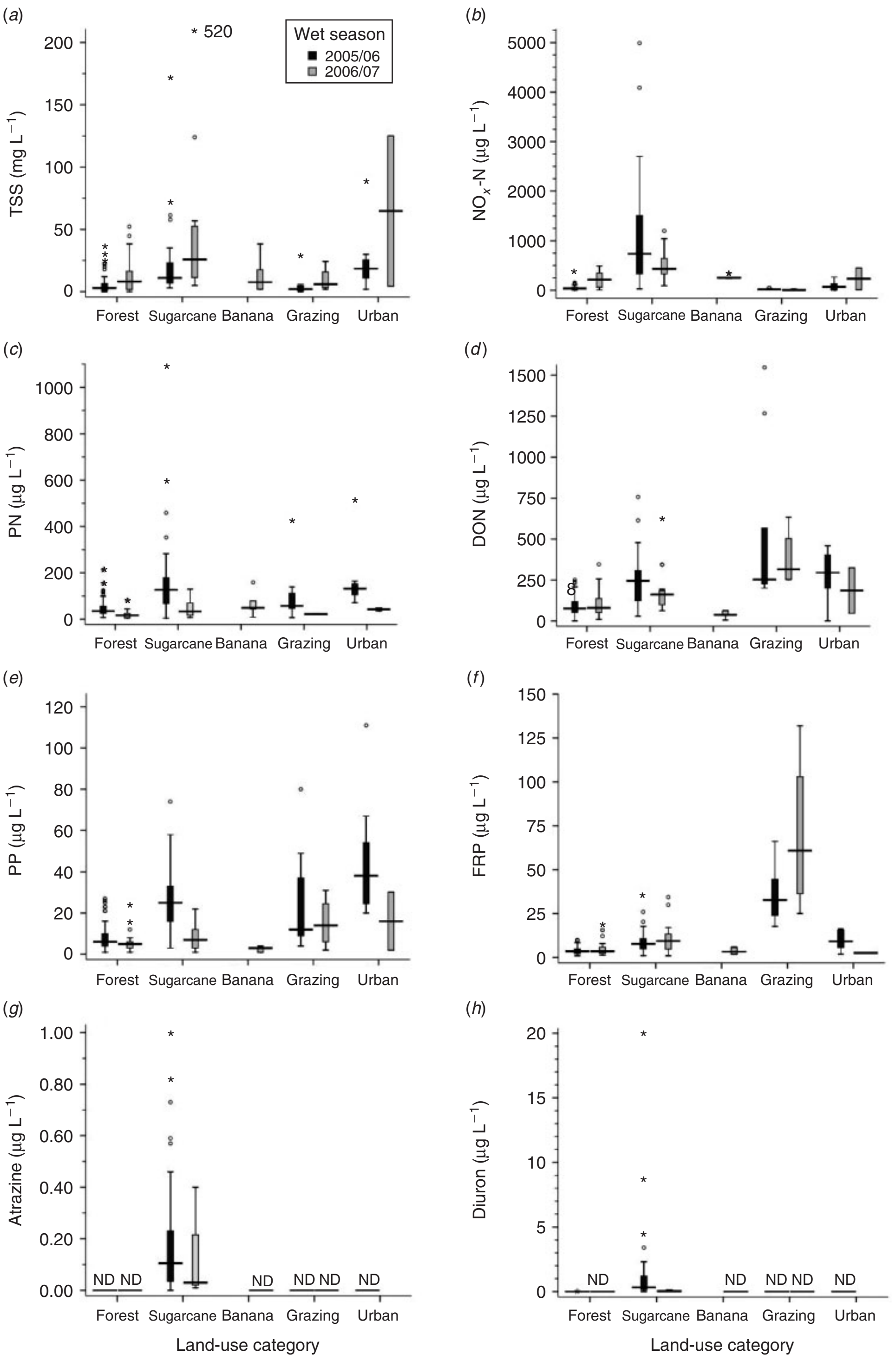

Fig. 2. Summary boxplots of (*a*) suspended sediment ($mg\,L^{-1}$), (*b*) oxidised nitrogen ($\mu g\,L^{-1}$), (*c*) particulate nitrogen ($\mu g\,L^{-1}$), (*d*) dissolved organic nitrogen ($\mu g\,L^{-1}$), (*e*) particulate phosphorus ($\mu g\,L^{-1}$), (*f*) FRP ($\mu g\,L^{-1}$), (*g*) atrazine ($\mu g\,L^{-1}$) and (*h*) diuron ($\mu g\,L^{-1}$) concentrations during the two wet season flood events across the major land use categories in the Tully–Murray basin. Median values are denoted by the horizontal line, with the box representing the inter-quartile range containing 50% of the data. The whiskers extend from the box to the highest and lowest concentrations, excluding outliers (circles), which are defined to be outside 1.5 box-lengths (outside the 25th and 75th percentiles) and extreme values (stars), which are defined to be outside 3 box-lengths. Samples analysed for atrazine (*g*) and diuron (*h*) residues that were below the analytical detection limit ($<0.01\,\mu g\,L^{-1}$) have been displayed as 'ND' (not detected).

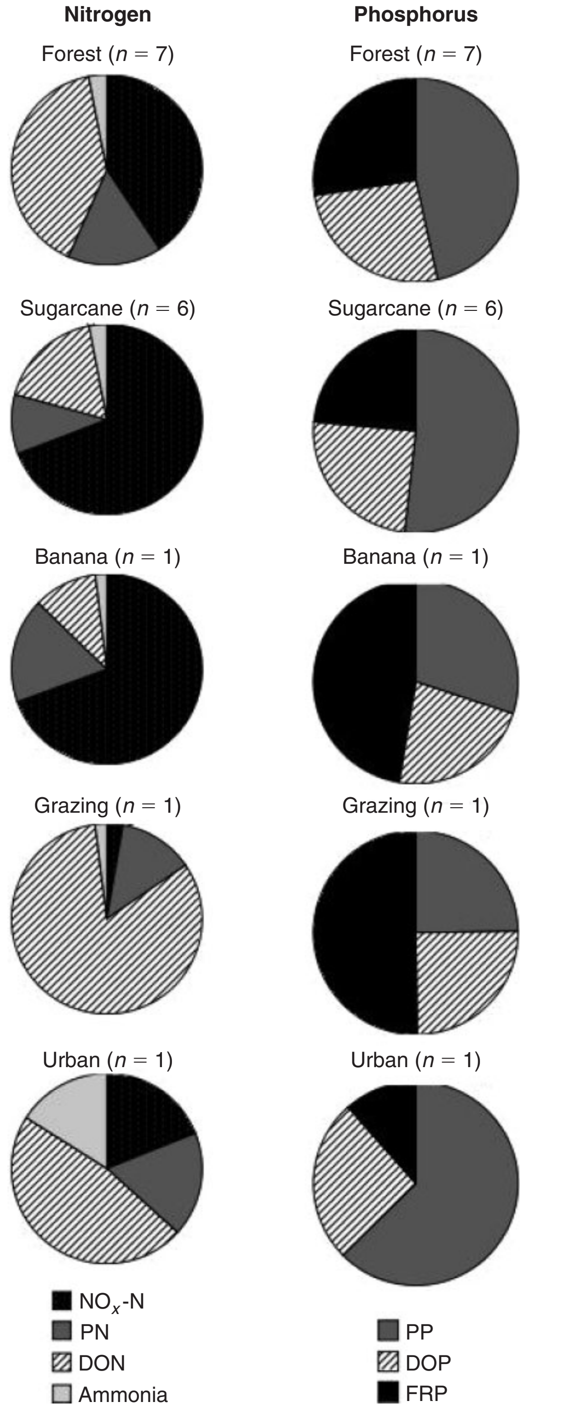

Fig. 3. Average proportion of nitrogen and phosphorus fractions for each land-use category. Fractions include particulate nitrogen (PN), particulate phosphorus (PP), dissolved organic nitrogen (DON), dissolved organic phosphorus (DOP), oxidised nitrogen (NO_x-N), ammonia and filterable reactive phosphorus (FRP). 'n' indicates the number of sites representing each land-use category.

concentrations only slightly elevated for the urban and sugarcane land-use categories compared with the forest land use (Fig. 2*a*). The introduction of green cane trash blanketing and minimum tillage practices over the past two decades by the sugarcane industry has resulted in considerable reductions in soil erosion from this land use (Rayment 2003). The range of SS concentrations found in this study (0.2–170 mg L^{-1}) are also consistent with the long-term dataset (10–250 mg L^{-1}) collected over the time periods 1989–1991 and 1995–2000 at the Tully River (Euramo) site (Mitchell and Furnas 2001; Mitchell *et al.* 2006). SS concentrations measured in this basin are lower than those measured in neighbouring catchments with similar rainfall regimes and land uses, including the Herbert River (range of 50–800 mg L^{-1}; Mitchell *et al.* 1997), Johnstone River (10–1200 mg L^{-1}; Hunter and Walton 2008) and Mackay Whitsunday catchments (5–1600 mg L^{-1}; range excludes a developing urban site; Rohde *et al.* 2008). The low SS concentrations measured in the Tully–Murray basin are indicative of lower erosion rates due to high ground cover resulting from regular, year-long rainfall and the location of intensive agriculture mainly on low slope areas of the floodplain. In contrast, SS concentrations are much higher in the Burdekin River catchment (20–14 000 mg L^{-1}; Bainbridge *et al.* 2007), which is dominated by rangeland beef grazing in a dry tropical rainfall regime, where ground cover is considerably lower leaving soils more exposed and erosion prone (e.g. Scanlan *et al.* 1996). Our results indicate that the run-off of SS is a relatively low concern in the Tully–Murray basin. However, a component of the SS load discharged from the Tully–Murray Rivers is transported to the adjacent inshore fringing reefs (Devlin and Brodie 2005) and may therefore influence turbidity on these reefs (see Wolanski *et al.* 2008).

The run-off of NO_x-N was particularly elevated in the sugarcane land-use category, which indicates the run-off of fertilisers applied by this industry (Fig. 2*b*). In both the sugarcane and banana land uses, NO_x-N contributed a high proportion (~70%) of TN compared with the other land uses (Fig. 3; see also Armour *et al.* 2009). Mitchell *et al.* (2009) demonstrated that a linear relationship exists between subcatchment NO_x-N concentrations and the percentage of fertiliser-additive land use in the upstream catchment area, proving the link to fertiliser application. The slightly elevated median NO_x-N concentration (250 μg L^{-1}) for the forest land use in the second wet season can be partially explained by several forest land-use sites that contain small areas of non-forest land uses, including sugarcane (0.6%) at Bulgun Creek, bananas (2.5%) at Jarra Creek and grazing/dairy (6.7%) at the Tully Gorge (Table 1). In comparison, the upstream Murray River (Murray Falls) site, which drains a catchment area only of natural forest, had a median NO_x-N concentration of 7 μg L^{-1} across the two monitored wet seasons, and is considered most representative of the forest land-use category. Typically the natural leakage of nitrogen is the dissolved organic fraction (Harris 2001; Perakis and Hedin 2002; Brodie and Mitchell 2005), with a shift to the more bioavailable inorganic fraction seen in fertilised cropping lands in neighbouring Wet Tropics catchments (e.g. Brodie and Mitchell 2005; Hunter and Walton 2008) and catchments worldwide (Carpenter *et al.* 1998). NO_x-N run-off has been found to disrupt downstream marine ecosystems (Fabricius 2005; Brodie *et al.* 2007) and has been linked to the degradation of coral reefs in many parts of the world (e.g. Lapointe *et al.* 2005). The highly elevated concentrations of NO_x-N (median ~600 μg L^{-1}) in the sugarcane-dominated subcatchments compared with natural forested subcatchments (e.g. Murray Falls;

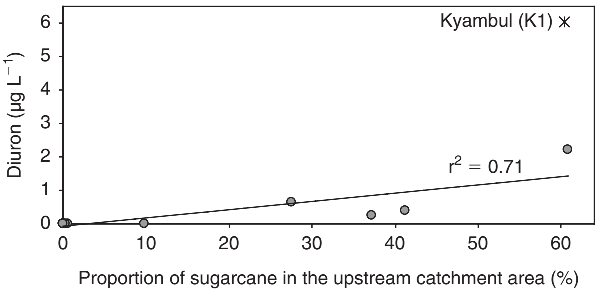

Fig. 4. Relationship between the mean diuron concentration ($\mu g\,L^{-1}$) for each subcatchment site over the two monitored wet seasons and the area of sugarcane land use in the upstream catchment.

median 7 $\mu g\,L^{-1}$) show that run-off from fertiliser intensive industries is a key water quality issue in the Tully–Murray basin.

The elevated concentrations of PN and DON in the sugarcane, grazing and urban land uses (Fig. 2*c*, *d*) likely reflect the location of these land uses on rich lowland soil types that also have a long history of nutrient enrichment through fertiliser use and mill mud application. The elevated ammonia concentrations detected at the urban land-use site (Fig. 3) may be associated with unsewered (septic) residential leachate as found in the neighbouring Johnstone River catchment (see Hunter and Walton 2008). The concentrations of all forms of phosphorus species were low across all land uses in the Tully–Murray basin and reflect the low soil erosion in the region, as phosphorus may be strongly bound to the soils (i.e. in the particulate form). Studies on selected soils in the adjacent Herbert River catchment have shown that the potential for phosphorus loss is generally not high (Bramley *et al.* 2003). One exception was the elevated FRP measured in the grazing land-use site, which may be associated with the application of superphosphate for improved pastures (Jones 1990).

The herbicides diuron, atrazine (including its degradation product desethyl atrazine) and hexazinone were frequently detected in waterways draining the sugarcane land use during both monitored wet seasons (Fig. 2*g*, *h*). Similarly to the relationship between nitrate concentrations and fertilised land use outlined in Mitchell *et al.* (2009), a linear relationship exists ($r^2 = 0.71$) between mean diuron concentrations and the proportion of sugarcane land use in the upstream catchment area (Fig. 4). This implies a fairly uniform application rate of these herbicides across the sugarcane industry within the Tully–Murray basin. A site at Kyambul (K1) proved to be an exception with a much higher mean concentration than the trend; this discrepancy may represent a sampling artefact with only four pesticide samples collected from this site. The herbicides detected in this study area are also utilised by the sugarcane industry in other GBR catchments, and have been commonly detected in subcatchment waterways associated with this land use (Rohde *et al.* 2008; Stork *et al.* 2008; Davis *et al.* in press). While the detection of diuron, atrazine, hexazinone and ametryn are all sourced to the sugarcane industry, simazine residues, detected only at the downstream Murray River site, are probably associated with plantation forestry (see McMahon *et al.* 2005) located in the upstream catchment area (Fig. 1). While simazine was detected at concentrations below the ANZECC and ARMCANZ (2000) ecological protection trigger value (99% species protection) of 0.20 $\mu g\,L^{-1}$, the run-off of this herbicide may become a water quality issue for the region with any future expansion of the plantation forestry industry.

The ANZECC and ARMCANZ (2000) ecological protection trigger value (low reliability guideline) for diuron (0.2 $\mu g\,L^{-1}$) was frequently exceeded. This indicates a potential risk to the freshwater bodies of the Tully–Murray basin, which include a series of wetlands listed on Australia's National Directory of Important Wetlands (ANCA 1996). To date, there have been limited ecotoxicological studies undertaken to assess the risk of herbicide exposure on northern Australian tropical freshwater and estuarine aquatic organisms (see Davis *et al.* in press). As such, the risk of these herbicides on downstream freshwater environments, including the potential cumulative effects resulting from the presence of several of these herbicides is largely unknown.

Herbicide residues in the Tully–Murray River flood plumes

Similarly to the catchment herbicide results, diuron also had the highest concentrations measured in the flood plumes. In the 2007 plume, diuron residues were detected at biologically significant concentrations 15 km from the river mouth to the extent of Dunk Island and the Family Island Group and associated fringing reefs and nearby seagrass beds. Detected concentrations exceeding LOEC of 0.1 $\mu g\,L^{-1}$ for the seagrass species *Halophila ovalis* and *Zostera capricorni* (Haynes *et al.* 2000*b*), and LOEC of 0.3 $\mu g\,L^{-1}$ for the coral species *Acropora formosa* and *Seriatopora hystrix* (Jones and Kerswell 2003) indicates a risk to coral and seagrass ecosystems within this inshore area (see also Lewis *et al.* 2009). Further, the impact of diuron on marine plants (e.g. coral zooxanthellae, seagrass, macroalgae) is likely to be enhanced by the additive effects that may result from the combination of this herbicide with residues of atrazine and hexazinone also detected in the plume, which, like diuron are photosystem II inhibitors (Jones *et al.* 2003; Bengtson Nash *et al.* 2005, 2006).

In conclusion, this monitoring program has identified both the water quality characteristics of the major land uses of the Tully–Murray basin as well as the water quality issues of concern to the region. The highly elevated run-off of NO_x-N from the sugarcane land use indicates the loss of fertiliser from intensive agricultural landscapes. This finding is consistent with previous studies and suggests that NO_x-N run-off is a key water quality issue in the region with the potential to disrupt downstream freshwater and marine ecosystems. The frequent detection of diuron, atrazine and hexazinone residues in the waterways draining sugarcane also indicate a risk to downstream freshwater and marine ecosystems where nationally derived ecological protection trigger values have been exceeded. These residues can be traced offshore as far as the Dunk Island and Family Island Group at concentrations known to have negative effects on seagrass and coral reef communities. The success of the WQIP is dependent on the management of these key pollutants identified in this study.

Acknowledgements

This study was supported by the Terrain Natural Resource Management Tully Water Quality Improvement Plan. We gratefully acknowledge the catchment field support provided by Laurence Liessmann, Shane Blowes and Vern Veitch (ACTFR) and David Green (Queensland Natural Resources and Water). Pesticide samples from the 2007 flood plume were collected in conjunction with Marine and Tropical Sciences Research Facility Projects 3.7.1 and 3.7.2, with acknowledgement to Dr Katharina Fabricius and Dr Tim Cooper (Australian Institute of Marine Science) for the collection of these samples. Acknowledgement is also extended to Dr Jochen Mueller (University of Queensland, National Research Centre for Environmental Toxicology) for supplying pesticide data from the 2006 flood plume and Dr Britta Schaffelke (AIMS) for the collection of these pesticide samples. Appreciation is given to QNRW and Bureau of Meteorology for access to stream flow and rainfall gauging station data. We would also like to acknowledge two anonymous reviewers for their improvements to the manuscript, and the Guest Editor (Dr Frederieke Kroon) for further helpful comments.

References

Anonymous (2003). Reef Water Quality Protection Plan: for catchments adjacent to the Great Barrier Reef World Heritage Area. Queensland Department of Premier and Cabinet, Brisbane. The State of Queensland and Commonwealth of Australia. Available at http://www.reefplan.qld.gov.au [verified 13 September 2009].

ANCA (1996). 'A Directory of Important Wetlands in Australia.' 2nd edn. (Australian Nature Conservation Agency: Canberra.)

ANZECC and ARMCANZ (2000). 'Australian and New Zealand Guidelines for Fresh and Marine Water Quality.' (Australian and New Zealand Environmental and Conservation Council, Agriculture and Resource Management Council of Australia and New Zealand: Canberra.)

Armour, J. D., Hateley, L. R., and Pitt, G. L. (2009). Catchment modelling of sediment, nitrogen and phosphorus nutrient loads with SedNet/ANNEX in the Tully–Murray basin. *Marine and Freshwater Research* **60**, 1091–1096.

APHA (2005). 'Standard Methods for the Examination of Water and Wastewaters.' 21st edn. (American Public Health Association, American Water Works Association and Water Environment Federation: Washington.)

Bainbridge, Z., Lewis, S., and Brodie, J. (2007). Event-based community water quality monitoring in the Burdekin Dry Tropics region: 2002–2007 (Vol 2). Australian Centre for Tropical Freshwater Research, James Cook University, ACTFR Report No. 07/22 for BDTNRM, Townsville, Qld. Available at http://www.actfr.jcu.edu.au/reports/2007/index.htm [verified 13 September 2009].

Bengtson Nash, S. M., McMahon, K., Eaglesham, G., and Müller, J. F. (2005). Application of a novel phytotoxicity assay for the detection of herbicides in Hervey Bay and the Great Sandy Straits. *Marine Pollution Bulletin* **51**, 351–360. doi:10.1016/J.MARPOLBUL.2004.10.017

Bengtson Nash, S. M., Goddard, J., and Müller, J. F. (2006). Phytotoxicity of surface waters of the Thames and Brisbane River estuaries: A combined chemical analysis and bioassay approach for the comparison of two systems. *Biosensors & Bioelectronics* **21**, 2086–2093.

Bramley, R. G. V., and Roth, C. H. (2002). Land-use effects on water quality in an intensively managed catchment in the Australian humid tropics. *Marine and Freshwater Research* **53**, 931–940. doi:10.1071/MF01242

Bramley, R. G. V., Roth, C. H., and Wood, A. W. (2003). Risk assessment of phosphorus loss from sugarcane soils – A tool to promote improved management of P fertiliser. *Australian Journal of Soil Research* **41**, 627–644. doi:10.1071/SR02099

Brodie, J. E., and Mitchell, A. W. (2005). Nutrients in Australian tropical rivers: changes with agricultural development and implications for receiving environments. *Marine and Freshwater Research* **56**, 279–302. doi:10.1071/MF04081

Brodie, J., De'ath, G., Devlin, M., Furnas, M., and Wright, M. (2007). Spatial and temporal pattern of near-surface chlorophyll *a* in the Great Barrier Reef lagoon. *Marine and Freshwater Research* **58**, 342–353. doi:10.1071/MF06236

Carpenter, S. R., Caraco, N. F., Correll, D. L., Howarth, R. W., Sharpley, A. N., and Smith, V. H. (1998). Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological Applications* **8**, 559–568. doi:10.1890/1051-0761(1998)008[0559:NPOSWW]2.0.CO;2

Davis, A., Lewis, S., Bainbridge, Z., Brodie, J., and Shannon, E. (in press). Pesticide residues in waterways of the lower Burdekin region: Challenges in ecotoxicological interpretation of monitoring data. *Australasian Journal of Ecotoxicology*.

DeVantier, L., De'ath, G., Turak, E., Done, T., and Fabricius, K. (2006). Species richness and community structure of reef-building corals on the nearshore Great Barrier Reef. *Coral Reefs* **25**, 329–340. doi:10.1007/S00338-006-0115-8

Devlin, M. J., and Brodie, J. (2005). Terrestrial discharge into the Great Barrier Reef Lagoon: nutrient behaviour in coastal waters. *Marine Pollution Bulletin* **51**, 9–22. doi:10.1016/J.MARPOLBUL.2004.10.037

Devlin, M., and Schaffelke, B. (2009). Spatial extent of riverine flood plumes and exposure of marine ecosystems in the Tully coastal region, Great Barrier Reef. *Marine and Freshwater Research* **60**, 1109–1122.

Fabricius, K. E. (2005). Effects of terrestrial runoff on the ecology of corals and coral reefs: review and synthesis. *Marine Pollution Bulletin* **50**, 125–146. doi:10.1016/J.MARPOLBUL.2004.11.028

Fabricius, K., De'ath, G., McCook, L., Turak, E., and Williams, D. McB. (2005). Changes in algal, coral and fish assemblages along water quality gradients on the inshore Great Barrier Reef. *Marine Pollution Bulletin* **51**, 384–398. doi:10.1016/J.MARPOLBUL.2004.10.041

Faithful, J., Brodie, J., Bainbridge, Z., Schaffelke, B., Slivkoff, M., Maughan, M., Liessmann, L., and Sydes, D. (2008). Water quality characteristics of water draining different land uses in the Tully/Murray Rivers region – Edition 2. Australian Centre for Tropical Freshwater Research, James Cook University, ACTFR Report No. 08/03 for Terrain NRM, Townsville, Qld. Available at http://www.actfr.jcu.edu.au/reports/2008/index.htm [verified 13 September 2009].

Furnas, M. (2003). 'Catchments and Corals: Terrestrial Runoff to the Great Barrier Reef.' (Australian Institute of Marine Science: Townsville, Qld.)

Great Barrier Reef Marine Park Authority (2009). Water quality guidelines for the Great Barrier Reef marine park. Great Barrier Reef Marine Park Authority, Townsville, Qld. Available at http://www.gbrmpa.gov.au/_data/assets/pdf_file/0016/33802/Water_Quality_Guidelines_for_the_GB R.pdf [verified 13 September 2009].

Harris, G. P. (2001). Biogeochemistry of nitrogen and phosphorus in Australian catchments, river and estuaries: effects of land use and flow regulation and comparisons with global patterns. *Marine and Freshwater Research* **52**, 139–149. doi:10.1071/MF00031

Haynes, D., Müller, J., and Carter, S. (2000*a*). Pesticide and herbicide residues in sediments and seagrasses from the Great Barrier Reef World Heritage Area and Queensland coast. *Marine Pollution Bulletin* **41**, 279–287. doi:10.1016/S0025-326X(00)00097-7

Haynes, D., Ralph, P., Prange, J., and Dennison, B. (2000*b*). The impact of the herbicide diuron on photosynthesis in three species of tropical seagrass. *Marine Pollution Bulletin* **41**, 288–293. doi:10.1016/S0025-326X(00)00127-2

Haynes, D., Brodie, J., Waterhouse, J., Bainbridge, Z., Bass, D., and Hart, B. (2007). Assessment of the water quality and ecosystem health of the Great Barrier Reef (Australia): Conceptual models. *Environmental Management* **40**, 993–1003. doi:10.1007/S00267-007-9009-Y

Hosomi, M., and Sudo, R. (1986). Simultaneous determination of total nitrogen and total phosphorus in freshwater samples using persulfate digestion. *International Journal of Environmental Studies* **27**, 267–275. doi:10.1080/00207238608710296

Hunter, H. M., and Walton, R. S. (2008). Land-use effects on fluxes of suspended sediment, nitrogen and phosphorus from a river catchment of the Great Barrier Reef, Australia. *Journal of Hydrology (Amsterdam)* **356**, 131–146. doi:10.1016/J.JHYDROL.2008.04.003

Hutchings, P., Haynes, D., Goudkamp, K., and McCook, L. (2005). Catchment to reef: water quality issues in the Great Barrier Reef region – an overview of papers. *Marine Pollution Bulletin* **51**, 3–8. doi:10.1016/J.MARPOLBUL.2004.11.026

Jones, R. J. (1990). Phosphorus and beef production in northern Australia. 1. Phosphorus and pasture productivity – a review. *Tropical Grasslands* **24**, 131–139.

Jones, R. J., and Kerswell, A. P. (2003). Phytotoxicity of photosystem II (PSII) herbicides to coral. *Marine Ecology Progress Series* **261**, 149–159 doi:10.3354/MEPS261149

Jones, R. J., Müller, J., Haynes, D., and Schreiber, U. (2003). Effects of herbicides diuron and atrazine on corals of the Great Barrier Reef, Australia. *Marine Ecology Progress Series* **251**, 153–167. doi:10.3354/MEPS251153

Kroon, F. J. (2009). Integrated research to improve water quality in the Great Barrier Reef region. *Marine and Freshwater Research* **60**, i–iii.

Lapointe, B. E., Barile, P. J., Littler, M. M., and Littler, D. S. (2005). Macroalgal blooms in southeast Florida coral reefs: II. Cross-shelf discrimination of nitrogen sources indicates widespread assimilation of sewage nitrogen. *Harmful Algae* **4**, 1106–1122. doi:10.1016/J.HAL.2005.06.002

Lewis, S. E., Brodie, J. E., Bainbridge, Z. T., Rohde, K., Davis, A., Masters, B., Maughan, M., Devlin, M., Mueller, J., and Schaffelke, B. (2009). Herbicides: A new threat to the Great Barrier Reef. *Environmental Pollution* **157**, 2470–2484. doi:10.1016/J.ENVPOL.2009.03.006

McMahon, K., Bengston Nash, S., Eaglesham, G., Müller, J. F., Duke, N. C., and Winderlich, S. (2005). Herbicide contamination and potential impact to seagrass meadows in Hervey Bay, Queensland, Australia. *Marine Pollution Bulletin* **51**, 325–334. doi:10.1016/J.MARPOLBUL.2004.10.045

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

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. doi:10.1071/MF96021

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

Mitchell, C., Brodie, J., and White, I. (2005). Sediments, nutrients and pesticide residues in event flow conditions in streams of the Mackay Whitsunday region, Australia. *Marine Pollution Bulletin* **51**, 23–36. doi:10.1016/J.MARPOLBUL.2004.10.036

Mitchell, A., Reghenzani, J., Furnas, M., De'ath, G., Brodie, J., and Lewis, S. (2006). Nutrients and suspended sediments in the Tully River: Spatial and temporal trends. Australian Centre for Tropical Freshwater Research, James Cook University, ACTFR Report No. 06/10, Townsville, Qld. Available at http://www.actfr.jcu.edu.au/reports/2006/index.htm [verified 13 September 2009].

Mitchell, A., Reghenzani, J., Faithful, J., Furnas, M., and Brodie, J. (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.

Perakis, S. S., and Hedin, L. O. (2002). Nitrogen from unpolluted South American forests mainly via dissolved organic compounds. *Nature* **415**, 416–419. doi:10.1038/415416A

Rayment, G. E. (2003). Water quality in sugar catchments of Queensland. *Water Science and Technology* **48**, 35–47.

Rohde, K., Masters, B., Fries, N., Noble, B., and Carroll, C. (2008). Fresh and marine water quality in the Mackay Whitsunday region 2004/05 to 2006/07. Queensland Department of Natural Resources and Water for MWNRM, Mackay, Qld. Available at http://www.nrw.qld.gov.au/science/projects/mackaywhitsunday/pdf/eventreport_april2008.pdf [verified 13 September 2009].

Scanlan, J. C., Pressland, A. J., and Myles, D. J. (1996). Run-off and soil movement on mid-slopes in north-east Queensland grazed woodlands. *The Rangeland Journal* **18**, 33–46. doi:10.1071/RJ9960033

Stork, P. R., Bennett, F. R., and Bell, M. J. (2008). The environmental fate of diuron under a conventional production regime in a sugarcane farm during the plant cane phase. *Pest Management Science* **64**, 954–963.

Wallace, J., Stewart, L., Hawdon, A., Keen, R., Karim, F., and Kemei, J. (2009). Flood water quality and marine sediment and nutrient loads from the Tully and Murray catchments in north Queensland, Australia. *Marine and Freshwater Research* **60**, 1123–1131.

Wilkinson, C. (Ed.) (2004). 'Status of Coral Reefs of the World.' (Australian Institute of Marine Science: Townsville, Qld.)

Wolanski, E., Fabricius, K. E., Cooper, T. F., and Humphrey, C. (2008). Wet season fine sediment dynamics on the inner shelf of the Great Barrier Reef. *Estuarine, Coastal and Shelf Science* **77**, 755–762. doi:10.1016/J.ECSS.2007.10.014

Manuscript received 2 December 2008, accepted 20 August 2009