Department of Natural Resources and Mines

Pesticides in groundwater of the Tully-Murray and Johnstone catchments

2012/2013 Report

Wet Tropics Region

Queensland Government

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Funding was provided by the Reef Water Quality Program (Project RP54C), DNRM and Terrain NRM from the Paddock to Reef Integrated Monitoring, Modelling and Reporting Program

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Acronyms and abbreviations

ANZECC - Australian and New Zealand Environment and Conservation Council
ARMCANZ - Agriculture and Resource Management Council of Australia and New Zealand
BoM - Bureau of Meteorology
DNRM - Department of Natural Resources and Mines
GBR - Great Barrier Reef
GCMS - Gas chromatography mass spectrometry
LCMS - Liquid chromatography mass spectrometry
NATA - National Association of Testing Authorities
NHMRC - National Health and Medical Research Council
NRMMC - National Resource Management Ministerial Council (Commonwealth of Australia)
PSII – Photosystem II (herbicides which inhibit photosystem II in plants include ametryn, atrazine, diuron and hexazinone)
P2R - Paddock to Reef Integrated Monitoring, Modelling and Reporting Program
QHFSS - Queensland Health and Forensic Scientific Services laboratory

Units

µg/L - micrograms per litre
mm - millimetres
ML - megalitre (1,000,000 litres)
ML/yr - megalitres per year
mAHD - metres above the Australian Height Datum (mean sea level)

EXECUTIVE SUMMARY

The coastal lowlands of the Wet Tropics region have been extensively modified for intensive agricultural production, with approximately 193,600 ha of sugarcane and 11,000 ha of bananas. Pesticides (herbicides, insecticides and fungicides) are important for the economic viability and sustainability of the sugarcane industry. However, the off-site movement of pesticides has been linked with the decline of water quality within the Great Barrier Reef (GBR) lagoon.

Under the Reef Water Quality Plan 2013, a target has been set to reduce the total transport of pesticides (particularly PSII herbicides) to the GBR by 60% by 2018. Progress towards these goals is measured through the Australian and Queensland government's *Paddock to Reef Integrated Monitoring, Modelling and Reporting Program* (P2R program). Currently catchment monitoring and modelling within the P2R program do not quantify all of the potential groundwater contributions to the GBR at end-of-system monitoring sites. Therefore, groundwater discharges and associated contaminant fluxes may be substantially under-represented within the program.

The aim of this project was to undertake a *preliminary* survey of groundwater quality within two catchments of the Wet Tropics region, the Tully-Murray and Johnstone. Research was funded by the Reef Water Quality Program (Project RP54C), Department of Natural Resources and Mines, and Terrain Natural Resource Management Ltd. from the P2R Program.

Groundwater bores were monitored at locations near existing *Paddock-scale Water Quality Monitoring* sites within the P2R program, in areas cropped for sugarcane and bananas. Each bore (up to seven) was sampled on three occasions to determine the temporal changes in groundwater before and after the wet season. Sampling was conducted in August and December (2012), and in April (2013). Samples were analysed for a broad range of pesticides including the PSII herbicides (diuron, atrazine and hexazinone); organochlorine and organophosphorus pesticides; synthetic pyrethroids; urea and triazine herbicides; phenoxyacid herbicides (e.g. 2,4-D) and glyphosate.

Rainfall during the study was generally below average. Each bore declined in water level from initial sampling in August through to December, corresponding with the low rainfall and therefore limited recharge. Following this dry period, water levels in most bores responded rapidly to rainfall, rising in the order of metres following each rainfall event and generally receding rapidly as groundwater discharged to streams. This indicates a very dynamic groundwater flow in the shallow unconfined aquifers (3-7 m), as well as the deeper aquifers (15-30 m), monitored in this study.

Nine herbicides and one insecticide were detected throughout the study. The most commonly detected herbicides (including the breakdown products of atrazine) were hexazinone (6 out of 7 bores), desethyl atrazine (5), propazin-2-hydroxy (5), atrazine (4), desisopropyl atrazine (4) and diuron (4). To a lesser extent the herbicides bromacil (2), simazine (2), metsulfuron methyl (1) and glyphosate (1) were also detected. The insecticide imidacloprid was detected in two bores and at the highest concentrations of all the pesticides within the study (1.5 µg/L).

In previous pesticide monitoring of the Johnstone catchment in 1995 and 1996 atrazine was present in four bores, with no other PSII herbicides detected in the 16 bores surveyed. Other herbicides, 2,4-D, MCPA and 2,4,5-T were also present, none of which was found in

this study. The limit of reporting was higher than those currently used by the laboratory, which is a common obstacle when comparing recent studies with previous research, as laboratory techniques for pesticide analysis have improved over time.

Bromacil, simazine, metsulfuron methyl and imidacloprid were only detected in bores within the Johnstone catchment. There was no detection of organochlorine or organophosphate pesticides, synthetic pyrethroids, or phenoxyacid herbicides (i.e. 2,4-D, picloram, triclopyr). Similarly, several herbicides with emerging use over recent years were tested and not detected (e.g. fluroxypyr, imazapic, isoxaflutole and trifloxysulfuron).

The pesticides detected in this study were also frequently detected in deep drainage leachate (1 m below the root zone) within the sugarcane and banana (glyphosate only) plots in the paddock-scale monitoring program. Furthermore, attention has been drawn to the potentially high losses of pesticides via the extensive network of constructed drains throughout sugarcane paddocks in the Wet Tropics region. It is likely that a major loss pathway for groundwater in sugarcane is through constructed drains, which is an area that is currently poorly understood.

The concentrations of pesticides detected in this study did not exceed Australian drinking water guideline values. In addition, a majority of pesticides did not exceed freshwater ecosystem guideline values. However, repeated sampling throughout both the wet and dry season indicated pesticide concentrations fluctuated over time, and in one bore diuron (0.3 µg/L) exceeded the freshwater ecosystem health guideline for protection of 95% of species (0.2 µg/L - low reliability trigger value).

The groundwater systems in the study area are highly dynamic and suggest short residence times before groundwater discharge into streams and drains (and more slowly to regional aquifers), and ultimately the Great Barrier Reef lagoon. This combination of dynamic systems and detention of a range of pesticides highlights the importance of an improved understanding in the Wet Tropics.

Priority research topics include:

- Expand the spatial extent of monitoring throughout the Johnstone and Tully-Murray, and include Mulgrave-Russell and Herbert catchments, and to a lesser extent Mossman and Lower Barron (based on size, landuse and contribution to the GBR).
- Identify sites within streams at groundwater discharge zones and conduct ambient monitoring to improve understanding of groundwater-surface water connectivity (base -flow).
- Conduct event sampling in drainage networks, particularly in conjunction with the new P2R phase 2 sugarcane monitoring site proposed for the Johnstone catchment at Silkwood.
- Increase catchment modelling capability of Source Catchments to incorporate groundwater-surface water connectivity.
- Update freshwater guideline values to incorporate the presence (toxicity) and additive effects of multiple pesticides.

These results were obtained during a period of below average rainfall. Thus, these results could be considered a minimum and as such the potential for higher losses to groundwater, and therefore higher concentrations of pesticides in groundwater, are possible in years of higher rainfall.

INTRODUCTION

The coastal lowlands of the Wet Tropics region have been extensively modified for intensive agricultural production, with approximately 193,600 ha of sugarcane and 11,000 ha of bananas grown in the region. In recent decades, pesticides (herbicides, insecticides and fungicides) have become important in the economic viability and sustainability of the sugarcane industry. In particular, herbicide use in sugarcane has contributed to the historic shift to a new farming system (Johnson and Ebert, 2000), which promotes green cane trash blanketing and minimum tillage practices. These practices have substantially reduced rates of soil erosion (Prove *et al*., 1995), which was previously perceived as the primary threat to the neighbouring World Heritage-listed Great Barrier Reef (Rayment, 2003). However, more recently the off-site movement of pesticides has also been linked with the decline of water quality within the Great Barrier Reef (GBR) lagoon (Lewis *et al.,* 2009).

Herbicides commonly used in the sugarcane industry, namely diuron, atrazine, ametryn and hexazinone, have been consistently detected in surface waters of catchments with sugarcane (Smith *et al.*, 2012; Bainbridge *et al.*, 2009; Lewis *et al.,* 2009), as well as in the coastal waters of the GBR lagoon (Shaw *et al*., 2010; Bainbridge *et al*., 2009; Lewis *et al*., 2009). The presence of these herbicides in marine ecosystems is of particular concern as they inhibit photosynthesis (PSII) and long-term chronic exposure may have adverse ecotoxicological effects on coral (Jones, 2005) and seagrass communities (Haynes *et al*., 2000a,b).

Under the Reef Water Quality Plan 2013 (Reef Plan, 2013), a target has been set to reduce the total export of pesticides (particularly PSII herbicides) to the GBR by 60% by 2018. This has been increased from the previous target of 50% in Reef Plan 2009. Progress towards these goals is measured through the Australian and Queensland governments' *Paddock to Reef Integrated Monitoring, Modelling and Reporting Program* (P2R program; Carroll *et al.*, 2012). Within this program the *GBR Catchment Loads Monitoring Program* conducts catchment-scale surface water quality monitoring of constituent loads at end-of-system sites in acute runoff events (e.g. Turner *et al.*, 2013). *Source Catchment* modelling (e.g. Wet Tropics, Hateley *et al*. 2014) provides estimates of end-of-system constituent loads for GBR natural resource management regions, and change of end-of-system loads due to land management practices. This modelling data is validated against the catchment monitoring data, as well as the data collected at the paddock scale.

Groundwater flows from water balance estimates in the Wet Tropics (Table 1) indicate a substantial contribution to stream and coastal waters from groundwater in these catchments. Pesticide residues have been also found in the groundwater systems of many GBR catchments including the lower Burdekin floodplain (Shaw *et al.*, 2012; Bauld, 1996), Pioneer Valley (Baskeran *et al.*, 2001), Bundaberg (Bauld, 1994), and to a limited degree the Wet Tropics (Hunter *et al*., 2001). Therefore, chronic exposure of Reef waters to groundwater sources of pesticides is a potential and unquantified threat. Currently the end-of-system monitoring sites do not capture all groundwater flows, or direct discharge to the coast, and could therefore substantially under-represent groundwater discharges and associated contaminant fluxes (Hunter, 2012). For example, in the Johnstone catchment there are substantial areas of sugarcane below the end-of-system site. However, various logistical factors restrict site selection, e.g. tidal influence, safety, accessibility (Hunter, 2012), and thus the area is not captured in the current sampling program.

The aim of this project was to undertake a *preliminary* survey of groundwater quality within two catchments of the Wet Tropics region, the Tully-Murray and Johnstone. This study is in conjunction with the P2R program and outlines monitoring results from three rounds of sampling in August and December 2012 and April 2013. Research was funded by the Reef Water Quality Program (Project RP54C), Department of Natural Resources and Mines, and Terrain Natural Resource Management Ltd. from the P2R Program.

Table 1. Draft water balance estimates of long-term mean annual groundwater discharges from Wet Tropics aquifers and comparisons with mean annual stream-flows (from Hunter, 2012).

Aquifer	**GW discharge to rivers, streams & drains** (ML/yr)	**GW discharge directly to the coast** (ML/yr)	**Total GW discharge to surface waters**[1] (ML/yr)	**Stream-flow**[2] (ML/yr)	**Total GW discharge as a proportion of stream-flow** (%)
Mulgrave-Russell [3]	99,300[4]	Not available	Not available	4,193,000	2.4
Johnstone[5]	289,616	2,726	292,342	4,698,000	6.2
Tully-Murray[6]	334,448	720	335,168	5,311,000	7.1
Herbert[7]	474,583	550	475,133	4,991,000	9.5

[1] Sum of two previous columns; [2] Hausler (1991); [3] GW data from DSITIA (2012a); [4] Average for two different irrigation scenarios; [5] GW data from DSITIA (2012b); [6] GW data from DSITIA (2012c); [7] GW data from DSITIA (2012d).

METHODOLOGY

Study location

The study was carried out in two of the coastal catchments of the Wet Tropics region, located south of Cairns in Queensland, Australia. Groundwater bores were selected in close proximity to the sugarcane and banana cropping paddock-scale water quality monitoring sites of the Paddock to Reef Monitoring and Evaluation program (Figure 1). The area has a tropical climate with hot wet summers (December to April) and mild winters (June to September). The study region encompassed bores in the Tully-Murray (Upper Murray) and Johnstone catchments. Average annual rainfall is 1,923 mm in the Upper Murray and 3,413 mm in the Johnstone (DNRM, 2013).

Bore selection and timing

This study was conducted as a preliminary survey of groundwater, with three bores to be sampled in each catchment where sugarcane and banana cropping are common (Table 2). Each bore was sampled on three occasions to determine the temporal changes in groundwater before and after the wet season. Sampling was conducted in August and December (2012), and in April (2013). Four bores were initially sampled in the Johnstone catchment in August 2012. However, bore 11210066 was found to have collapsed and although initial samples were collected and analysed, no further sampling was conducted. Three bores were initially sampled in the Tully-Murray catchment, but bore 1400024 was poor yielding and only sampled once (August 2012). Details of all the bores sampled are provided in Appendix A.

Table 2. Percentage of banana and sugarcane in the Johnstone and Tully-Murray catchments

Catchment	Banana		Sugarcane	
	(km^2)	**(% of total area)**	**(km^2)**	**(% of total area)**
Johnstone	66	3	280	12
Tully-Murray	72	3	361	13

(Source Catchments: Hateley *et al.* 2014)

Sample collection

Samples were collected in accordance with *AS/NZS 5667.11:1998-Australian/New Zealand Standard Water quality-Sampling Part 11: Guidance on sampling of groundwaters.* Bores were purged of their total volume three times and then sampled after electrical conductivity, dissolved oxygen, Eh (redox state), pH and temperature had stabilised, using a geocontrolPRO groundwater sampling bladder pump. Two litres of water was collected in solvent rinsed amber glass bottles. Samples were stored on ice (<4°C) in insulated boxes in the field and transferred to refrigerated storage each day. The samples were shipped via overnight transport on ice to the Queensland Health Forensic and Scientific Services (QHFSS) laboratory.

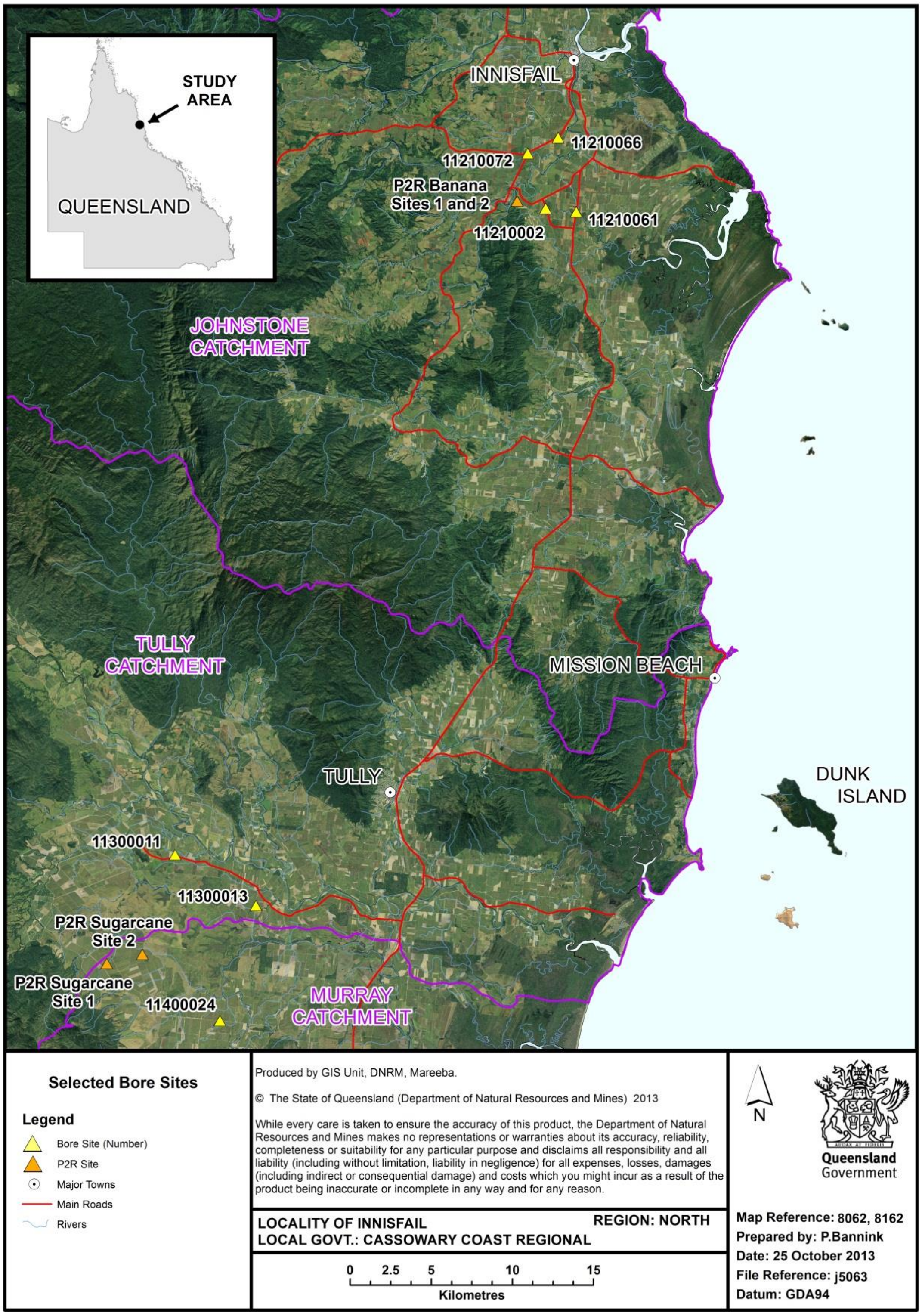

Figure 1. Location of groundwater bores sampled in the Johnstone and Tully-Murray catchments

Groundwater level

Solinst Leveloggers were deployed in three bores (11300013 and 11300011 in the Tully-Murray catchment; and 11210061 in the Johnstone catchment) from December to April, and removed when final samples were collected. Depth and temperature data were obtained on a 15 minute time step. One Solinst Barologger was deployed in each region to measure atmospheric pressure. This was used to compensate the water level data. Data was then referenced to sea level height (mAHD).

Bore level data in bore 11210002(A) was provided by the Hydrographic group, DNRM, South Johnstone, whilst bore level data at 11210072 was provided by James Cook University. Solinst Leveloggers were also used to collect data in both of these bores.

Laboratory analyses

All water samples were analysed by the Queensland Health and Forensic Scientific Services laboratory in Brisbane, Queensland for analysis (QHFSS, accredited by National Association of Testing Authorities, NATA).

Samples were analysed for:
Method (16315) – Organochlorine (OC) pesticides, Organophosphorus (OP) pesticides, Synthetic Pyrethroids, Urea, Triazine herbicides, PCBS in water by GCMS/LCMS
Method (16631) – Phenoxyacid Herbicides in water by LCMS
Method (29937) – Herbicide (Low level) in water by SPE/LCMSMS
Method (26601) – Glyphosate, AMPA and glufosinate in water by SPE and LCMSMS

Samples collected in December (the driest period) were not analysed for phenoxyacid herbicides or glyphosate. Selected compounds and their physical chemical properties are listed in Table 3. The full list of compounds included in the analysis is provided in Appendix B.

The unfiltered water samples were analysed by liquid chromatography mass spectrometry (LCMS) and gas chromatography mass spectrometry (GCMS). Organochlorine, organophosphorus and synthetic pyrethroid pesticides, urea and triazine herbicides and polychlorinated biphenyls were extracted from the sample with dichloromethane. The dichloromethane extract was concentrated before measurement by GCMS and LCMS (QHFSS method number 16315). Phenoxyacid herbicide water samples, which were collected in separate 1 litre amber glass bottles, were acidified and extracted with diethyl-ether. After evaporation and methylation, the samples were extracted with petroleum ether and analysed by GCMS (QHFSS method number 16631).

Table 3. Selected properties of compounds analysed taken from the footprint pesticide properties database (University of Hertfordshire, 2013).

Analyte	Soil Half lives	Soil sorption coefficient (K_{oc})	Log K_{ow}	GUS Leaching potential Index[b]
Pesticides by LCMSMS				
Ametryn	37	316	2.98	2.35
Atrazine	29	100	2.7	3.3
Bromacil	60[a]	32	1.88	3.44
Diuron	89	1,067	2.87	1.83
Fluometuron	89.8	-	2.28	3.92
Hexazinone	105[a]	54	1.17	4.58
Imidacloprid	174	-	0.57	3.76
Metolachlor	21	120	3.4	3.49
Prometryn	41 a	400	3.34	0.59
Simazine	90	130	2.3	2.00
Tebuthiuron	400 a	80	1.79	5.46
Terbutryn	52	2,432	3.66	2.40
Desethyl atrazine (DEA)	45 a	73	1.51	3.54
Phenoxy herbicides				
Dicamba	3.9	-	-1.88	2.63
Mecoprop	8.2 a	47	-0.19	2.29
MCPA	25	74	-0.81	2.51
2,4-DP (Dichlorprop)	10	74	2.29	2.39
2,4-D	10	88.4	-0.83	1.62
Triclopyr	30	27	4.62	3.69
MCPB	7 a	-	1.32	1.66
Fluroxypyr	51	-	0.04	0.00
2,4-DB	15.6	224	1.35	1.99
Picloram	36	13	-1.92	6.03
Clopyralid	11	5	-2.63	5.06
Fenoprop (2,4,5-TP)	14[a]	2,600	3.8	0.67
2,4,5-T	350[a]	-	4.0	-
Total Haloxyop	9 a	75	-	2.03
Pesticides by GCMS				
Metribuzin	19	-	1.65	2.57
Pendimethalin	90	17,581	5.2	-0.39
Diazinon	18.4	609	3.69	1.14
Chlorpyrifos	21	8,151	4.7	0.15
Propiconazole	214	1,221	3.72	1.51
Glyphosate by LCMSMS				
AMPA (Aminomethylphosphonic Acid)	151	8027	-1.63	0.21
Glufosinate (acid)	ND[c]	ND	-3.96	ND
Glyphosate	12	1,435	-3.2	-0.49

Note: Only selected compounds included in the GCMS pesticides screen are listed as these are known to be in use in cane growing areas of the Great Barrier Reef. Grey shaded cells indicates selected chemicals detected in this study.

[a] Typical value instead of field value.

[b] Groundwater Ubiquity Score (GUS) is a methodology used to estimate the potential for a pesticide to move into groundwater. It is calculated from the soil half-life (note: caution is required as values were not derived for WT soils) and partition coefficient (K_{ow}). GUS = log t ½ x (4-log K_{ow}) where K_{oc} is the soil sorption coefficient (mL/g) and the t ½ is the half-life in soil (days). Higher values indicate greater potential for leaching (range <0.1 - > 4.0). GUS values lower than 1.8 and higher than 2.8 indicate, respectively, non-leacher and leacher pesticide compounds; for GUS values between 1.8 and 2.8 the pesticide is considered in a transition zone (Gustafson, 1989).

[c] ND – no data available in the PPDB

RESULTS and DISCUSSION

Rainfall and groundwater recharge

Rainfall during the study was generally below average (Aug 2012 – April 2013). The period of below average rainfall between August and December was broken with a 163 mm rainfall event at the end of December. Following this, a majority of the rain fell over four days in late January (i.e. 700 mm at South Johnstone and 550 mm in the upper Murray), and then in early April in both the Tully-Murray (Figure 2) and Johnstone catchments (Figure 3).

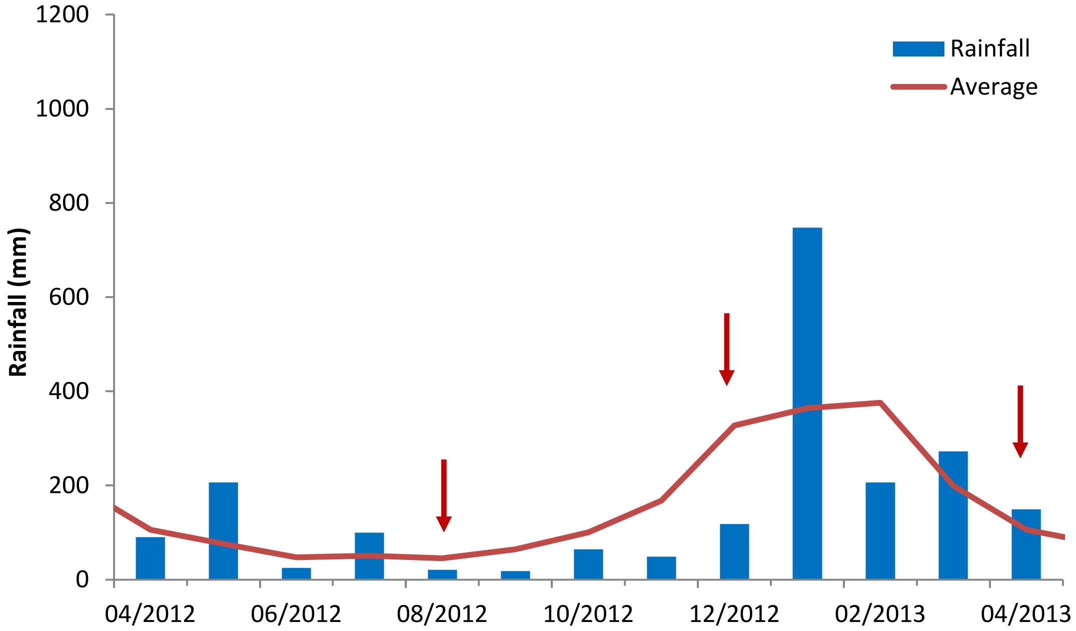

Figure 2. Total monthly rainfall recorded at Tully-Murray (P2R sugarcane Site 2)
Note: Arrows indicate sampling events

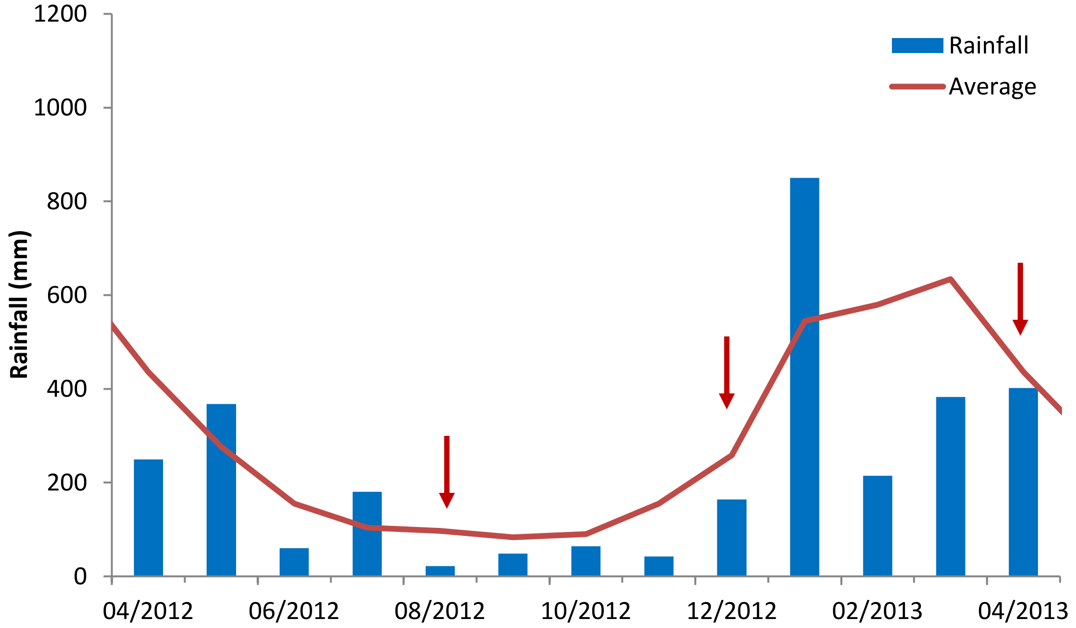

Figure 3. Total monthly rainfall recorded at South Johnstone Research Station
Note: Arrows indicate sampling events

Water level in each bore declined from initial sampling in August through to December, corresponding with the low rainfall and therefore limited recharge (Figure 4 to Figure 8). Following this dry period, water levels in most bores responded rapidly to rainfall, rising in the order of metres following each rainfall event and generally receding rapidly as groundwater discharged to streams. The largest response was measured in bore 11210002 within the Johnstone catchment (Figure 5), which increased by 6 m almost immediately following the large rainfall event (700 mm) at the end of January. There were also signs of frequent irrigation extraction followed by quick recovery in this bore. Bore 11210002 was also the deepest bore in the study (screen at 29.5-31.5 m). Similarly the shallower bores had sharp, but smaller increases in water level in response to the large rainfall event. Water level in these shallower bores tended to recede faster than the deeper bores. This indicates a very dynamic groundwater flow in the shallow unconfined aquifers (3-7 m), as well as the deeper aquifers (15-30 m), monitored in this study. This would be representative of most typical groundwater systems in the Wet Tropics (Hunter, 2012). An outline of aquifer characteristics in catchments of the Wet Tropics can be found in Appendix C.

Occurrence of pesticides

Nine herbicides (hexazinone, atrazine, propazin-2-hydroxy, diuron, bromacil, simazine, metsulfuron methyl and glyphosate) and two breakdown products of the herbicide atrazine (desethyl atrazine (DEA) and desisopropyl atrazine) were detected at least once in the three rounds of sampling of five bores (Table 4, note two additional bores sampled in August). The insecticide imidacloprid was detected in two of the groundwater bores sampled.

Bromacil, simazine, metsulfuron methyl and imidacloprid were only detected in bores within the Johnstone catchment (Figure 4 to Figure 6). There was no detection of organochlorine or organophosphate pesticides, synthetic pyrethroids, or phenoxyacid herbicides (i.e. 2,4-D, picloram, triclopyr). Similarly, several herbicides with emerging use over recent years were tested and not detected (e.g. fluroxypyr, imazapic, isoxaflutole and trifloxysulfuron).

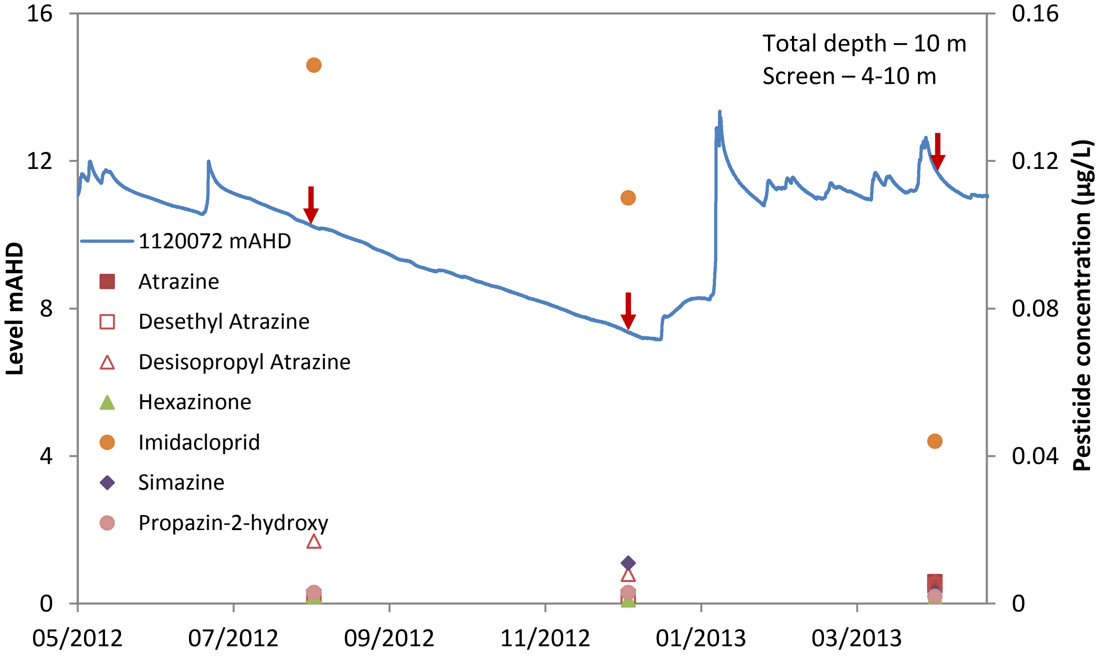

Figure 4. Pesticide concentrations and water level in bore 1120072 (Johnstone catchment)
Note: Arrows indicate sampling events. Limit of Report (LOR) = 0.005 μg/L.

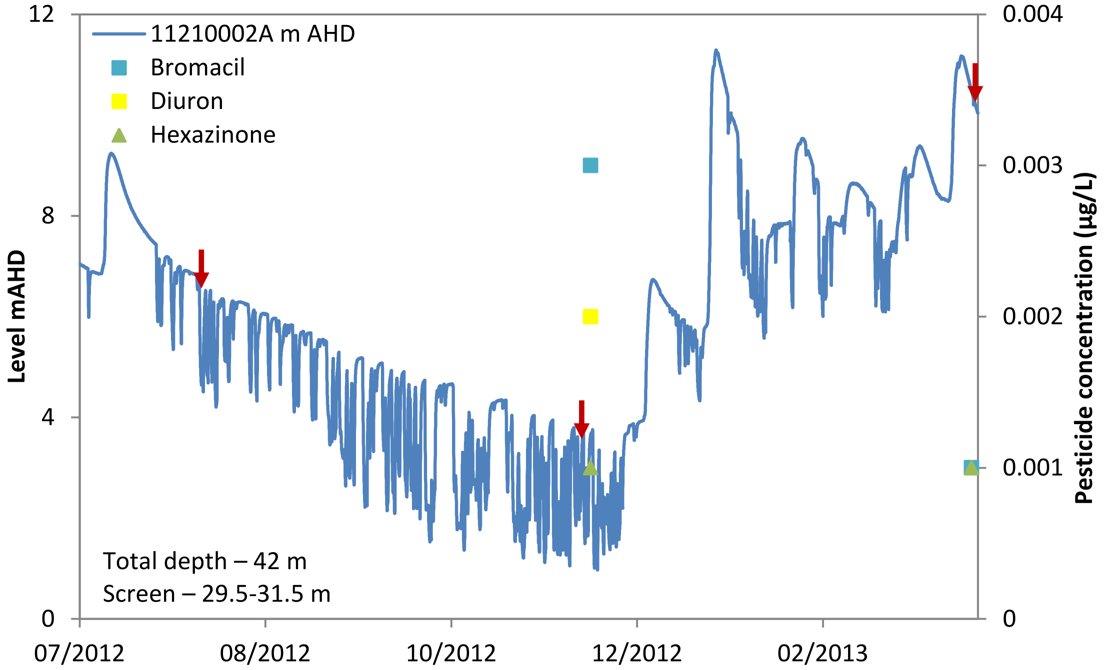

Figure 5. Pesticide concentrations and water level in bore 11210002 (Johnstone catchment)
Note: No pesticides above detectable limits in August 2012; arrows indicate sampling events.
LOR = 0.005 µg/L

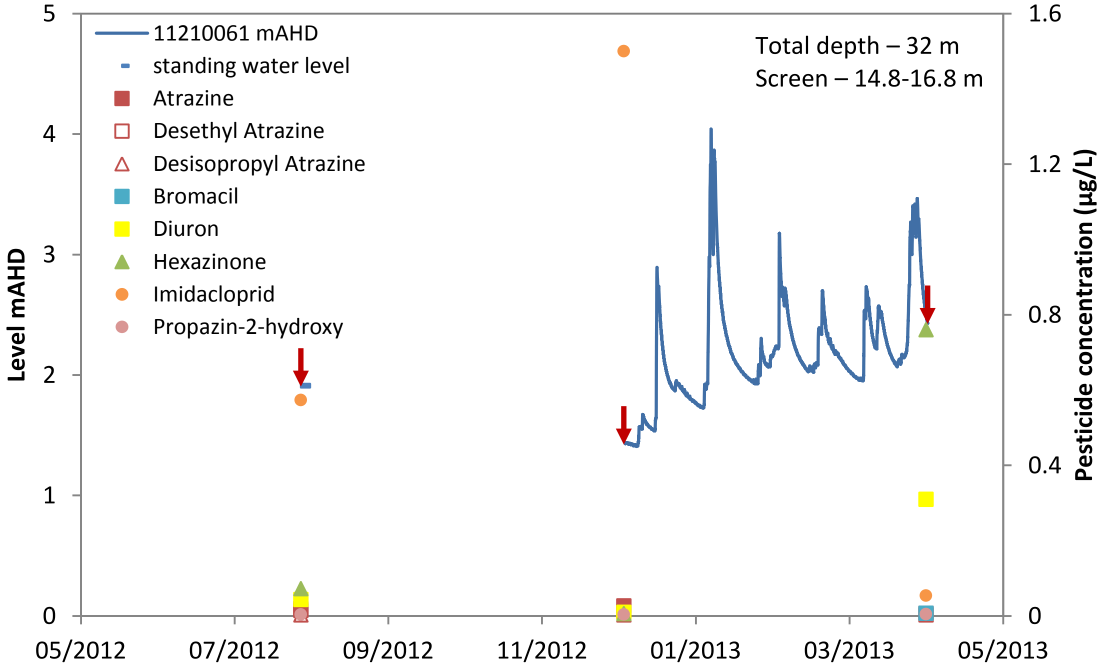

Figure 6. Pesticide concentrations and water level in bore 11210061 (Johnstone catchment)
Note: Arrows indicate sampling events. LOR = 0.005 µg/L

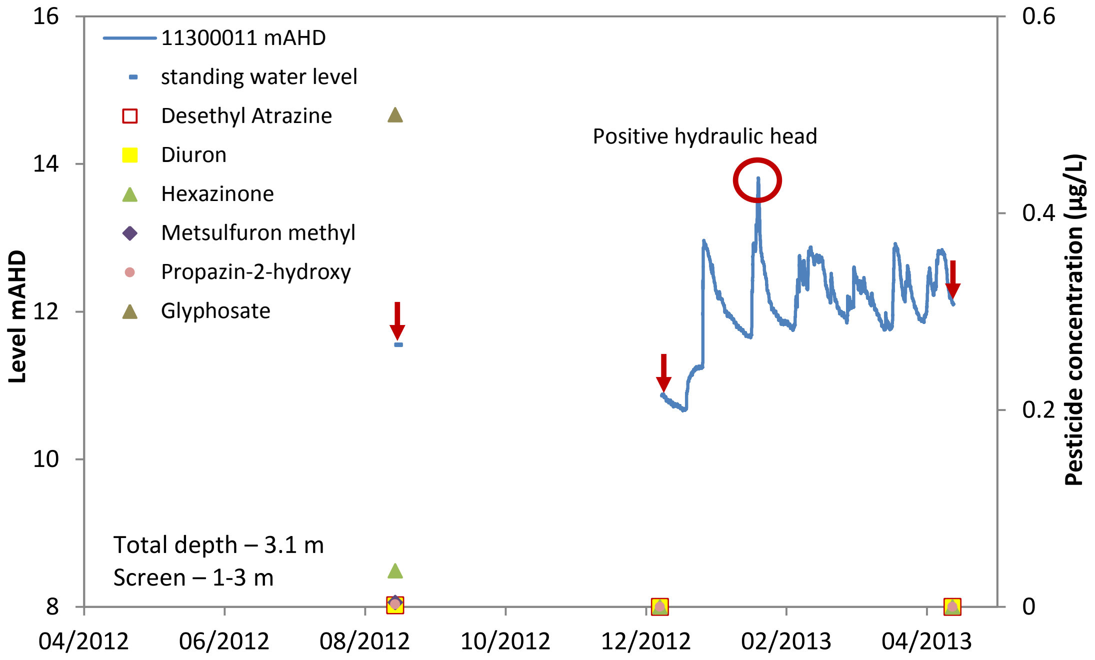

Figure 7. Pesticide concentrations and water level in bore 11300011 (Tully-Murray catchment)
Note: Arrows indicate sampling events. LOR = 0.005 µg/L

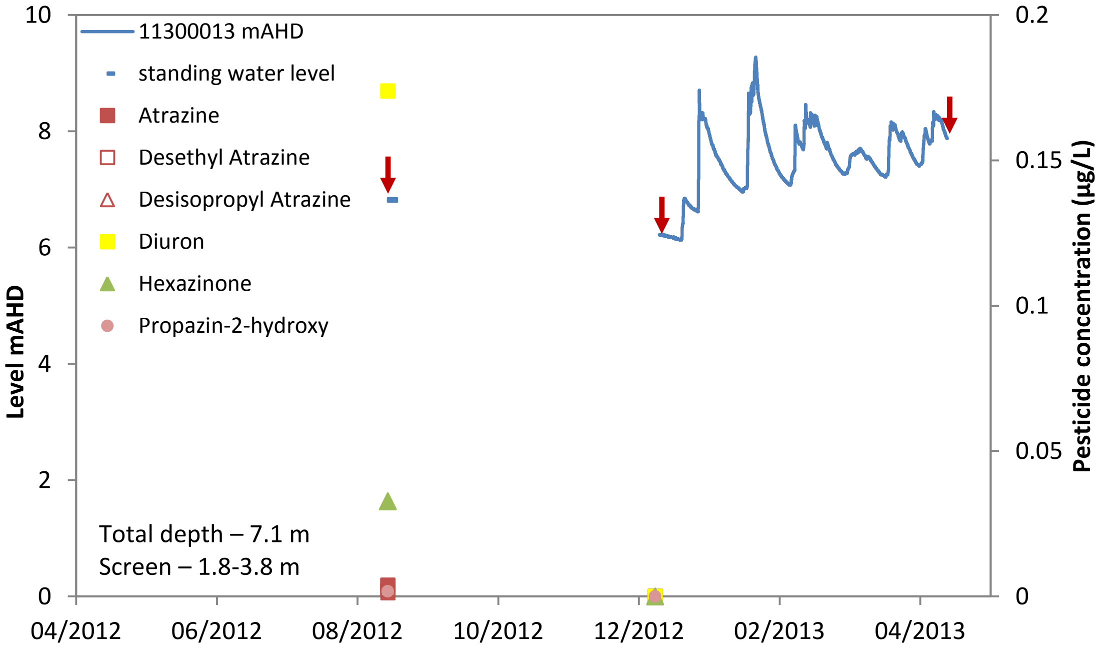

Figure 8. Pesticide concentrations and water level in bore 11300013 (Tully-Murray catchment)
Note: No pesticides above detectable limits in August 2012; arrows indicate sampling events.
LOR = 0.005 µg/L (note: glyphosate = 0.5 µg/L)

Table 4. Summary of results for Wet Tropics groundwater pesticide analysis

Analyte	Freshwater Guideline Value (ANZECC[a]) (µg/L)	Health Value (ADWG[b]) (µg/L)	Public Health Regulation Standard[c] (µg/L)	August 2012 (7 bores)			December 2012 (5 bores)			April 2013 (5 bores)		
				No. of detections	Concentration (µg/L)		No. of detections	Concentration (µg/L)		No. of detections	Concentration (µg/L)	
					Max	Mean		Max	Mean		Max	Mean
Pesticides by LCMSMS (LOR = 0.005 µg/L)												
Atrazine	13	20	40[d]	3	0.019	0.013	2	0.027	0.015	2	0.006	0.005
Bromacil	-	400	300	0	BD	BD	1	0.003	0.003	2	0.007	0.004
Desethyl Atrazine (DEA)	-	-	40[d]	5	0.051	0.015	4	0.011	0.004	3	0.007	0.004
Desisopropyl Atrazine	-	-	40[d]	5	0.017	0.007	2	0.008	0.006	2	0.006	0.005
Diuron	0.2	20	30	4	0.174	0.056	4	0.015	0.007	2	0.310	0.162
Hexazinone	75	400	300	5	0.073	0.031	5	0.027	0.007	4	0.760	0.212
Imidacloprid	-	-	-	2	0.573	0.360	2	1.5	0.805	2	0.054	0.049
Simazine	3.2	20	20	1	0.012	0.012	1	0.011	0.011	1	0.003	0.003
Metsulfuron methyl	-	40	30	1	0.005	0.005	0	BD	BD	0	BD	BD
Propazin-2-hydroxy	-	50[e]	50[e]	5	0.004	0.003	4	0.004	0.003	3	0.005	0.003
Glyphosate/Glufosinate (LOR = 0.5 µg/L)												
Glyphosate	1200	1000	1000	1	0.500	0.500	NA	NA	NA	0	-	-

Note: Only pesticides which were detected in groundwater are listed. LOR = Limit of report, NA = no analysis, BD = below detectable limits

[a] Australian and New Zealand Guidelines for Fresh and Marine Water Quality (*ANZECC and ARMCANZ 2000), freshwater trigger value for protection of 95% of species. Low reliability trigger values have been included.

[b] Australian Drinking Water Guidelines 6 (HNMRC and NRMMC 2011)

[c] Queensland Public Health Regulation (2005) - Schedule 3B - Standards for quality of recycled water supplied to augment a supply of drinking water

[d] Atrazine (total) including metabolites

[e] Health Value for Propazine

There were only three instances when pesticide residues were not detected. These were bore 11210002 and 11400024 in August 2012, and bore 11300013 in April 2013. In all other samples analysed, there was at least three or more pesticides above reporting limits. The most commonly detected herbicides (including the breakdown products of atrazine) were hexazinone (6 out of 7 bores), DEA (5), propazin-2-hydroxy (5), atrazine (4), desisopropyl atrazine (4) and diuron (4). The herbicides bromacil (2), simazine (2), metsulfuron methyl (1) and glyphosate (1) were also detected less frequently. Imidacloprid was consistently detected in two bores (1121006 and 1120072; Johnstone catchment) and at the highest concentrations of all the pesticides within the study. The metabolite of glyphosate, AMPA, was not detected. The three known metabolites of diuron, DCPMU (1-(3,4-dichlorophenyl)-3-methylurea), DCPU (1-3,4-dichlorophenylurea) and DCA (3,4-dichloroaniline) were not included in the analysis.

Typically the shallower bores had more pesticides present, at higher concentrations than pesticides in the deeper bores. For example, there were three herbicides present below 0.004 µg/L in bore 11210002 (the deepest bore), compared with six chemicals up to 0.5 µg/L in bore 11300011. Some pesticide residues were not always detected in each sampling round of the same bore (e.g. bromocil in bore 11210002, metsulfuron methyl and glyphosate in bore 11300011). This may suggest that the low concentrations within groundwater are close to laboratory reporting limits and slight fluctuations in concentration result in nil detection. This is an important consideration for groundwater studies which can be restricted to once off sampling events.

In previous pesticide monitoring of the Johnstone catchment (1995 and 1996) the only PSII herbicide detected was atrazine (0.2-0.7 µg/L; 4 bores) in the 16 bores surveyed (Hunter *et al.*, 2001). In addition, 2,4-D, MCPA and 2,4,5-T were also present, none of which were found in our study. The limit of reporting was higher than those currently used by the laboratory, which is a common obstacle when comparing recent studies with previous research, as laboratory techniques for pesticide analysis have improved over time. A majority of concentrations measured in our study are below the detection limits of the methods used in 1995 and 1996 (atrazine, 0.1 µg/L; hexazinone, 0.2 µg/L; propazine, 0.02 µg/L; simazine, 0.05 µg/L; diuron, 0.5 µg/L; glyphosate, 20 µg/L; and 2,4-D, 0.22 µg/L). Chemicals not included in the 1995/1996 analytical suite which were detected in this study included imidacloprid, bromacil and metsulfuron methyl. Out of the 16 bores sampled in 1995 and 1996, bore 11210072 was the only one which overlapped with our study and only 2,4-D (0.34 µg/L) was detected in 1995.

A general comparison of these results (all bores in both studies) showed that atrazine concentrations have declined in the last 17 years (0.2 to <0.03 µg/L) and that recently 2,4-D has not been detected at all. This is despite the fact 2,4-D is still regularly used in sugarcane (Armour *et al.*, 2013). This may suggest a shift in product choice and/or method of application in recent years, or perhaps lower rainfall during this study. The metabolites of atrazine were more commonly found than the parent compound, and samples collected in the Johnstone generally had high DEA/atrazine concentration ratios, which may also reflect the declining use of atrazine within these catchments (typically lower concentrations of the metabolite compared to the parent compound suggests rapid leaching, higher concentrations of the metabolite suggest no recent introduction of atrazine).

To put our results into current context, a comparison with a recent groundwater study in the Lower Burdekin floodplain (cropped with sugarcane) found only four herbicides including atrazine, diuron, hexazinone and metolachlor (plus atrazine's metabolites), and the organophosate insecticide chlorpyrifos (Shaw *et al*., 2012). In that study, DEA (17 bores, 32%) and desisopropyl atrazine (11, 21%) were the most commonly detected herbicides out of 53 bores monitored, followed by atrazine (7, 3%), hexazinone (4, 7.5%), diuron (2, 3.8%) and metolachlor (1, 1.9%). Markedly fewer bores were sampled in the current study (though more frequently), but a much larger percentage of bores had detectable concentrations of hexazinone (85.7%), propazin-2-hydroxy (71.4%), DEA (71.4%), desisopropyl atrazine (57.1%) and diuron (57.1%). Furthermore, the pesticides imidacloprid, bromacil, simazine, and metsulfuron methyl were not found in the Lower Burdekin groundwater. These differences are likely to reflect differences in land use and regional product preferences (although imidacloprid has been detected in the surface waters (0.008 µg/L) of Barratta creek in the Lower Burdekin; Shaw *et al*., 2012) in addition to the higher average annual rainfall, and strong groundwater-surface water connectivity in the Wet Tropics.

Deep drainage and groundwater connectivity

Pesticides were also monitored in deep drainage with barrel lysimeters at 1 m depth (below the root zone) within the P2R paddock scale monitoring sites on sugarcane (upper Murray; Armour *et al*., 2013) and bananas (South Johnstone; Masters *et al*., 2014), during the same study period (Table 5). At the sugarcane sites the most commonly detected chemicals in groundwater were also frequently detected in drainage leachate. For imidacloprid and diuron, this was approximately 2 ½ years after they were applied (at Site 1). There were no recent records for the application of atrazine or simazine, although they were found at above reporting limits in leachate at both sites. Deep drainage samples were not analysed for pesticides for the 2010/11 wet season, so it is therefore likely pesticide concentrations would have been higher during this time, as it was closer to the time of application. When these chemicals are transported to the subsurface, there is reduced capacity for biodegradation as a result of decreased soil organic matter and microbial activity at depth. Therefore, they have the potential to reside in subsurface environments for extended periods of time. Moreover, once drainage has passed the root zone of the crop it is unable to be managed by the landholder, and therefore is susceptible to uncontrolled loss.

There is an extensive and deep network of constructed drainage channels throughout the farms monitored in the P2R program in the Wet Tropics (>1.5 m deep; Figure 9). These are designed to lower the water table by quickly draining groundwater from paddocks, protecting crops from waterlogging damage (Hunter, 2012). Note that the groundwater level in the bores monitored were typically at <1 to 2 m below the ground surface during the wet season (Appendix A, Table 7). In the Tully-Murray there is an estimated 1,100 km of these constructed drainage networks (Armour *et al.,* 2007). Constructed drains are also prevalent in the Johnstone and Mulgrave-Russell catchments. Initial water balance estimates indicate the main pathway of groundwater discharge in the Mulgrave-Russell is via drains with approximately 92,000-98,000 ML/yr, compared with total annual discharge to rivers of 1,700-5,100 ML/yr (DSITIA, 2012a). To date sampling of drains has not been incorporated into the P2R program due to resource limitations. Sampling at P2R Sugarcane Site 2 was regularly hampered by an ephemeral perched water table, due to a clay pan at 0.9 m depth. This would submerge the lysimeter barrels within the perched water and as a result drainage volumes could not be determined during these periods. There was strong reason to believe the major loss pathway of this perched water, and associated pesticides, was via lateral flow to the constructed drains nearby. However, samples were not collected in the drainage network (Armour *et al*., 2013). On ground observations of farming practices (i.e. drainage networks) and soil types in the Tully-Murray catchment suggest that lateral flow to drains is a dominant loss pathway.

Table 5. Summary of pesticides detected in deep drainage (1 m below the root zone) in the P2R Sugarcane (from Armour *et al*., 2013) and Banana monitoring sites (Masters *et. al*., 2014).

Analyte	**Concentration range (µg/L) & (No. of detections)**		
	Sugarcane (Site 1)	**Sugarcane (Site 2)**	**Banana (Site 2)**
(Sampling conducted between November 2011 – March 2013)	25-27% deep drainage (of rainfall) Site approx. 50 m from an ephemeral stream. Legume fallow	Ephemeral perched water table (approx. 30 cm). Deep constructed drains on farm (>1.5 m). Watermelon fallow.	30-33% deep drainage (of rainfall and irrigation) Bare inter-row maintained with herbicides.
Imidacloprid	0.022-0.09 (10)	0.02-0.05 (9)	N/A
Diuron	0.005-0.02 (7)	0.02-0.02 (2)	N/A
Tebuconazole	0.1-0.3 (6)	BD	N/A
Simazine	0.003-0.02 (3)	0.002-0.03 (3)	N/A
Atrazine	0.001-0.002 (2)	0.02-0.02 (2)	N/A
Propazin-2-hydroxy*	0.002-0.003 (2)	0.003-0.003 (2)	N/A
Hexazinone	0.001-0.01 (2)	0.02 (1)	N/A
Flusilazole*	0.001-0.002 (2)	BD	N/A
2,4-D*	0.004 (1)	0.014-0.15 (2)	N/A
Terbutryn	BD	0.002-0.01 (3)	N/A
Metolachlor	0.002 (1)	0.002-0.03 (3)	N/A
Triclopyr*	BD	0.005-0.008 (2)	N/A
MCPA*	BD	0.005 (1)	N/A
Glyphosate	NS	NS	0.8-1.1 (2)
AMPA	N/A	N/A	BD
Glufosinate-ammonium	N/A	N/A	BD
Mancozeb	N/A	N/A	BD

Note: Grey shaded cells indicate pesticides detected in groundwater (this study). Parentheses indicate frequency of detection (sampling on fortnightly basis depending on rainfall). NS = not sampled. BD = below detection limit. Samples collected in sugarcane sites from 2013 were analysed by a solid phase extraction followed by LCMS (Method 29937) which improved reporting limits (<0.01 to <0.001 μg/L) and the scope of pesticides analysed*. Sugarcane sites were located on separate farms in the Upper Murray, and the Banana Site was located in South Johnstone.

Figure 9. A constructed drain within a sugarcane field in the Tully-Murray catchment

The detection of the herbicide glyphosate, regularly used by multiple industries, agricultural and non-agricultural, in both groundwater (this study) and deep drainage (Masters *et al.*, 2014) has highlighted the potential for a theoretically highly sorbing chemical to move into subsurface environments. Glyphosate has strong sorption properties (Table 3) and hence high adsorption to the soil matrix has been assumed to reduce mobility. This characteristic coupled with the perception that it has a short persistence, has favoured glyphosate as a 'low risk' alternative to longer-lived pre-emergent herbicides, such as diuron. However, a growing body of evidence suggests that glyphosate may be leached from the root zone into drainage water and groundwater systems. Vereecken (2005) reported that glyphosate associated with the colloidal fraction may find its way into drainage water via preferential flow paths, after high rainfall events and shortly after application. At the P2R banana site, glyphosate was detected in deep drainage after the large rainfall event in January (700 mm over four days, 100 mm drainage). However, this was more than six months after application. In this study, glyphosate was detected on one occasion in a shallow bore (Figure 8) next to sugarcane in the Tully-Murray. It is unknown whether glyphosate had been used around the base of the bore cap for weed control (a common practice on edges and fences lines), which would increase the chance of subsurface movement through preferential flow around the case of the bore. Nevertheless, these results highlight the potential for downward movement of glyphosate. It should be noted the analytical reporting limit of glyphosate is higher than most other pesticides (0.5 µg/L vs 0.001 µg/L).

Human health implications

The concentrations of pesticides detected in this study did not exceed Australian drinking water guideline values (Table 4; NHMRC and NRMMC 2011). However, there are no guideline values developed for imadicloprid, which was the only pesticide detected above 1 µg/L. The Australian drinking water guideline values have been derived from the acceptable daily intake (ADI) and are set at about 10% of ADI for an adult weight of 70 kg and daily water consumption of 2 litres (NHMRC and NRMMC 2011). It should be noted that sampling was not conducted in bores throughout the Lower Mulgrave-Russell catchment. This region has extensive alluvial development for sugarcane production and the Cairns City Council has a significant allocation for town water supply. This knowledge gap underlines the need for monitoring in this catchment.

Environmental implications

Water quality guidelines for the protection of groundwater dependent ecosystems are not available. However, freshwater ecosystem guideline values (ANZECC and ARMCANZ, 2000) can be used as an appropriate standard in this circumstance due to the close aquifer-stream connections, in addition to irrigation water quality guidelines for crop damage (ANZECC and ARMCANZ, 2000). Pesticide concentrations generally did not exceed either of these guidelines, with the exception of diuron (0.3 µg/L) which did exceed the freshwater ecosystem health guideline for protection of 95% (0.2 *µ*g/L - low reliability trigger value) of species. This occurred in one bore in April 2013 (post wet season). Pesticide concentrations in samples in August and December were below the guideline values. This emphasises the need for regular sampling during wet and dry seasons.

There are no Australian freshwater ecosystem guidelines for the insecticide imidacloprid, which was found in the highest concentrations of all pesticide detected (1.5 µg/L). However, this value did exceed the interim freshwater guideline (0.23 µg/L) set in the Canadian Water Quality Guidelines for the Protection of Aquatic Life (CCME, 2007). Imidacloprid has also shown high chronic toxicity to freshwater mayfly nymphs (Roessink *et al.*, 2013). Outside of a water quality context, there is increasing global concern of the use of imidacloprid, and the European Commission has placed restrictions on its use to protect honey bee populations (Mole *et al.*, 2013).

Glyphosate does not appear to be as prevalent in deep drainage or groundwater compared to the PSII herbicides, although it has been detected on limited occasions. Glyphosate has lower toxicity for aquatic plants, algae, crustaceans, invertebrates and fish than diuron (University of Hertfordshire, 2013) and therefore may continue to be a safer alternative to the PSII herbicides.

Guideline values have only been applied to individual pesticides. However, in this study more than three pesticides were usually present. The presence of more than one PSII herbicide has been shown to act in an additive manner for photosystem II inhibition (Lewis *et al*., 2012). Some metabolites were not analysed (e.g. for diuron), which in some cases can be of higher toxicity than the parent material (e.g. DCPMU compared with diuron) and the combined presence of both compounds together would have a greater impact (Stork *et al*., 2008).

Gaps and future activities

This initial investigation has highlighted the presence of several pesticides in groundwater, as well as highly dynamic groundwater flow, suggesting quick recovery and potentially short residence times between groundwater recharge and movement into streams and drains, and ultimately the Great Barrier Reef lagoon. Repeated sampling throughout wet and dry seasons has also indicated these pesticide concentrations fluctuate over time. Future studies should focus on a larger spatial coverage of bores to determine the extent of pesticides in groundwater throughout the Johnstone and Tully-Murray as well as other catchments within the Wet Tropics region, particularly the Mulgrave-Russell and Herbert (refer to Appendix C, Table 14 for key aquifer features). Further information is also needed on the linkages of groundwater to base-flow (during event and ambient conditions) in streams and drains, as well as connectivity to the reef (via streams or directly to the coast). It is likely that a major loss pathway for groundwater in sugarcane is through constructed drains, which is an area that is currently poorly understood.

Priority research topics include:

- Expand the spatial extent of monitoring throughout the Johnstone and Tully-Murray, and include Mulgrave-Russell and Herbert catchments, and to a lesser extent Mossman and Lower Barron (based on size, landuse and contribution to the GBR).
- Identify sites within streams at groundwater discharge zones and conduct ambient monitoring to improve understanding of groundwater-surface water connectivity (base -flow).
- Conduct event sampling in drainage networks, particularly in conjunction with the new P2R phase 2 sugarcane monitoring site proposed for the Johnstone catchment at Silkwood.
- Increase catchment modelling capability of Source Catchments to incorporate groundwater-surface water connectivity.
- Update freshwater guideline values to incorporate the presence (toxicity) and additive effects of multiple pesticides.

CONCLUSIONS

Sampling of up to seven bores in the Tully-Murray and Johnstone catchments on three occasions from August 2012 to April 2013 indicated the herbicides atrazine (including metabolites), hexazinone, propazin-2-hydroxy, diuron, simazine, metsulfuron methyl and glyphosate were all present at least once. The insecticide imidacloprid was detected on two occasions. When pesticides were detected, more than three pesticides were usually present in samples from the same bore.

These results were obtained during a period of below average rainfall. Thus, these results could be considered a minimum and as such the potential for higher losses to groundwater, and therefore higher concentrations of pesticides in groundwater, are possible in years of higher rainfall. Groundwater recharge after rainfall was rapid, followed by quick recession indicating fast discharge to streams and drains. Pesticide concentrations fluctuated prior to and shortly after wet season rainfall, with diuron exceeding the freshwater ecosystem health guideline for protection of 95% of species on one occasion. Other pesticides did not exceed Australian freshwater ecosystem guideline values.

Given the proximity to the Great Barrier Reef World Heritage area it is recommended that sampling should be expanded and continued on a regular basis.

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APPENDIX A

Table 6. Location and description of sampled bores in the Johnstone and Tully-Murray catchments

Bore Number	Latitude	Longitude	Total depth (m)	Screen (m, top-bottom)	Aquifer characteristic (bed lithology)
Tully-Murray					
11300011	-17.968725	145.808651	3.1	1-3	Clay & sand
11300013	-17.996965	145.853454	7.1	1.8-3.8	Sand, gravel & silt
11400024	-18.060674	145.833456	3.1	1.1-3.1	Sand & clay
Johnstone					
11210072	-17.579912	146.004107	10	4-10	Clay
11210066	-17.57113	146.020994	NR	34.2-36.2	NR
11210061	-17.612319	146.03095	32	14.8-16.8	NR
11210002	-17.610365	146.013997	42	29.5-31.5	Coarse sand (SJ River Alluvium)

Note: NR = No record

Table 7. Standing water level of bores*

Standing Water(m)	August 12	December 12	April 13
Tully-Murray			
11300011 (0.33)	1.74	2.43	1.21
11300013 (0.48)	2.94	3.54	2.05
11400024 (0.38)	1.75	NS	NS
Johnstone			
11210072 (0.28)	3.54	6.44	2.4
11210066 (0.30)	4.94	NS	NS
11210061 (0.29)	2.97	3.45	2.46
11210002 (0.31)	5.49	8.46	1.81

Note: NS = No sample *= Depth to water level from casing edge (casing height in parenthesis)

Table 8. Land use surrounding bore casing

Bore number	Local land use
Tully-Murray	
11300011	Road reserve, sugarcane, and creek with riparian vegetation
11300013	Sugarcane and road reserve
11400024	Sugarcane and rail reserve
Johnstone	
11210072	Railway, park, road reserve and sugarcane
11210066	Sugarcane and rail reserve
11210061	Main road and sugarcane
11210002	Banana, rail and road reserve (high water extraction?)

APPENDIX B

Table 9. Herbicides included in QHFSS SPE/LCMSMS (Low Level) analysis

Herbicides
Ametryn
Atrazine
Bromacil
Desethyl Atrazine
Desisopropyl Atrazine
Diuron
Fluometuron
Hexazinone
Imidacloprid
Metolachlor
Prometryn
Simazine
Tebuthiuron
Terbutryn
2,4-D
2,4-DB
Acifluorfen
Clomazone
Cyanazine
Ethametsulfuron methyl
Fluroxypyr
Flusilazole
Haloxyfop (acid)
Imazethapyr
Isoxaflutole
MCPA
MCPB
Mecoprop
Mesosulfuron methyl
Metsulfuron methyl
Napropamide
Propachlor
Propazin-2-hydroxy
Sethoxydim (including Clethodim)
Sulfosulfuron
Terbuthylazine
Terbuthylazine desethyl
Total Imazapic
Triclopyr
Trifloxysulfuron

Table 10. Herbicides included in QHFSS GCMS analysis

Herbicides
Ametryn
Amitraz
Atrazine
Bromacil
Desethyl Atrazine
Desisopropyl Atrazine
Diclofop-methyl
Fluazifop-butyl
Fluometuron
Haloxyfop-2-etotyl
Haloxyfop-methyl
Hexazinone
Metolachlor
Metribuzin
Molinate
Oxyfluorfen
Pendimethalin
Prometryn
Propanil
Propazine
Simazine
Tebuthiuron
Terbuthylazine
Terbutryn
Triallate
Trifluralin

Table 11. Herbicides included in the QHFSS phenoxyacid screen using LCMS.

Phenoxyacid Herbicides
2,4,5-T
2,4,5-TP
2,4-D
2,4-DB
2,4-DP
Clopyralid
Dicamba
Fluroxypyr
Haloxyfop
MCPA
MCPB
Mecoprop
Organics Env. Lab #
Picloram
Triclopyr

Table 12. Herbicides included in the QHFSS glyphosate screen using SPE and LCMSMS

Herbicides
AMPA (Aminomethylphosphonic Acid)
Glufonsinate (acid)
Glyphosate
Organics Env. Lab #
Total Glyphosate

Table 13. Pesticides included in the QHFSS broad screen using GCMS/LCMS

Organochlorine Pesticides
Aldrin
Chlordane cis
Total Chlordane
Chlordane trans
Chlordene
Chlordene epoxide
Chlordene-1-hydroxy
Chlordene-1-hydroxy-2,3-epoxide
Dicofol
Dieldrin
Endosulfan alpha
Endosulfan beta
Endosulfan ether
Endosulfan lactone
Endosulfan sulfate
Endrin
Endrin aldehyde
HCB
HCH alpha
HCH beta
HCH delta
Heptachlor
Heptachlor epoxide
Lindane (<gamma>-HCH)
Methoxychlor
Nonachlor cis
Nonachlor trans
DDD (op)
DDE (op)
DDT (op)
Oxychlordane
DDD (pp)
DDE (pp)
DDT (pp)
Total Aldrin & Dieldrin
Total DDT
Total Endosulfan
Total Heptachlor

Organophosphorus Pesticides
Azinphos-ethyl
Azinphos-methyl
Bromophos-ethyl
Cadusafos
Carbophenothion
Chlorfenvinphos
Chlorpyrifos
Chlorpyrifos oxon
Chlorpyrifos-methyl
Coumaphos
Demeton-S-methyl
Diazinon
Dichlorvos
Dimethoate
Dioxathion
Disulfoton
Ethion
Ethoprophos
Etrimphos
Famphur
Fenamiphos
Fenchlorphos
Fenitrothion
Fenthion (methyl)
Fenthion-ethyl
Isofenphos
Malathion (Maldison)
Methidathion
Mevinphos
Monocrotophos
Omethoate
Oxydemeton-methyl
Parathion (ethyl)
Parathion-methyl
Phorate
Phosmet
Phosphamidon
Pirimiphos-methyl
Profenofos
Prothiofos
Pyrazophos
Sulprofos
Temephos
Terbufos
Tetrachlorvinphos
Total Dimethoate

Other compounds (analysed by GCMS)
1H-Benzotriazole
1H-Benzotriazole, 1-methyl
1H-Benzotriazole, 5-methyl
2,6-Di-t-butyl-p-cresol (BHT)
2,6-Di-t-butylphenol
4-Chloro-3,5-dimethylphenol
Bisphenol A
Galaxolide
Moclobemide
Musk Ketone
Musk Xylene
N-Butylbenzenesulfonamide
N-Butyltoluenesulfonamide
Tonalid
Tri-n-butyl phosphate
Triclosan
Triclosan methyl ether
Triethyl phosphate
Tris(chloroethyl) phosphate
Tris(chloropropyl) phosphate isomers
Tris(dichloropropyl) phosphate
Other Pesticides
Benalaxyl
Bendiocarb
Bitertanol
Captan
Carbaryl
Chlorothalonil
DEET
Dimethomorph
Fipronil
Furalaxyl
Metalaxyl
Methoprene
Oxadiazon
Piperonyl butoxide
Pirimicarb
Procymidone
Propargite
Propiconazole
Propoxur
Rotenone
Tebuconazole
Tetradifon
Thiabendazole
Total Triadimefon
Triadimefon
Triadimenol
Vinclozolin

Synthetic Pyrethroids
Bifenthrin
Bioresmethrin
Cyfluthrin
Cyhalothrin
Cypermethrin
Deltamethrin
Fenvalerate
Fluvalinate
Permethrin
Phenothrin
Tetramethrin
Transfluthrin

Pesticides (analysed by GCMS)
1H-Benzotriazole
Aldrin
Amitraz
Azinphos-ethyl
Benalaxyl

APPENDIX C

Table 14. Summary of key features of aquifers in the Wet Tropics (from Hunter, 2012).

Groundwater area	Description
Daintree River	There is some alluvial development in the lower reach of the river. Groundwater discharge provides continuous baseflow to the river[1].
Mossman River	A shallow, low storage aquifer that receives high recharge. Groundwater discharge continuously to the river[2]; area under cane decreasing due to urban encroachment[1].
Lower Barron River (0-19 km AMTD)	Is section of the river receives groundwater inflows and is perennial (and mostly tidal)[1,2].
Lower Mulgrave & Russell Rivers (0-32 km AMTD) Area approx. 325 km ^{2}	The area has extensive alluvial development for sugarcane production, with minimum irrigation[1]. Cairns City Council has a significant allocation for town water supply. The alluvial sequence is composed of silty/sandy sediments[2]. The alluvium has an average thickness of 45 m. The aquifers consist of poorly sorted sand and gravel, with the main aquifers located 15-45 m below the ground surface. Fractured bedrock and basalt aquifers also occur. The potentiometric surface varies from the groundwater to approx. 13 m depth. Draft water balance estimates indicate discharge to drains is the main pathway of groundwater discharge (approx. 92,000-98,000 ML/yr depending on irrigation extractions), compared with total annual discharge to rivers of 1,700-5,100 ML/yr)[3].
Lower Johnstone River (0-38 km AMTD) (including Moresby R., Liverpool Ck. & Maria Cks.) Area approx. 1,755 km^2	This is a major cane-producing area with high rainfall. Little water is used for cane irrigation, but expansion of banana industry has increased irrigation demand. Surface water and groundwater are closely linked[1,2]. There are significant thickness of alluvium (max. thickness >80 m) and basalt (of variable thickness, max. >90 m). The texture of the alluvium is heterogeneous and includes heavy clays, coarse sands and gravels, but much of it is clayey, clay-bound sands or gravel. Most alluvium appears to behave as a single unconfined unit. Large and rapid response of groundwater levels to rainfall occur in some bores, followed by rapid recession, indicating close aquifer-stream connections. Artificial drainage networks occur in some areas to reduce water logging of cane. Draft water balance estimates indicate the total annual groundwater discharge to rivers, streams and drains is 289,616 ML/yr, and to the coast, 2,7726 ML/yr[4].
Lower Tully River (0-30 m AMTD) & Murray River Area approx. 1,470 km^2	A high rainfall; major crops area sugarcane and bananas (grown with negligible irrigations). An extensive artificial network of drains lowers shallow groundwater levels to reduce waterlogging. Rivers and streams area groundwater fed and perennial[1]. The alluvium ranges in thickness (max. >60 m) and comprises varying proportions of clay, silt, sand and gravel, much of it is clayey. Most of the alluvium appears to respond as a single unit and shows marked seasonality. A deeper semi-confined aquifer unit occurs in some areas. Recharge of the alluvium occurs directly via rainfall percolation through soils and through transient stream recharge during high stream flows. Groundwater discharge occurs as baseflow to rivers and streams, as discharge to the drainage network (e.g. in the Murray-Riversdale area), as seepage to coastal wetlands and as through-flow to the coast[5].

Groundwater area	**Description**
Lower Herbert River (0-80 km AMTD) Area approx. 1,530 km^2	Extensive alluvial plains; a major sugarcane production area, with some parts artificially drained to lower watertables; irrigation use is not extensive but groundwater is used for some urbane water supplies; groundwater and surface water systems are closely connected[1,2]. Management issues include saltwater intrusion, acid sulphate soils, declining watertables near wetlands, and pollution from chemical leaching near recharge areas[2]. The alluvial stratigraphy of the Herbert River delta comprises 4 aquifers at different depths and of differing water quality, with three aquifers predominately confined and the fourth (uppermost) unconfined. The uppermost aquifer is recharged directly from rainfall, with groundwater levels fluctuating seasonally between approx. 1.5 m and 3.1 m depth. The most extensive and thickest sand unit within the alluvium has an average depth of 25 m; at least one of two mud units in the alluvium is of marine origin. Overall, the natural surface drainage of streams traversing the alluvium is to act as groundwater drains except during transient periods of high stream flow when they act to locally recharge groundwater, which is subsequently and rapidly drained back into the river[6].

1EHA (2006); [2]KCB (2009); [3]DSITIA (2012a); [4]DISITA (2012b); [5]DISITA (2012c); [6]Cox (1979) cited by DSITA (2012d); [7]DISITA (2012d).

Note: AMTD = Adopted middle thread distance. Distance in kilometres from the mouth of the water course. Grey shaded areas indicate the catchments monitored in this study (Johnstone bores were in the South Johnstone). Other catchments within the Wet Tropics have been included to show relative contributions, which may aid in prioritising future monitoring activities.