Department of Environment and Resource Management

Pesticides in groundwater of the Lower Burdekin floodplain

March 2012

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Disclaimer

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Preface

Through the Raising National Water Standards Program, the National Water Commission (NWC) provided funding to the former Queensland Department of Environment and Resource Management (DERM) to develop a groundwater modelling toolkit for the aquifers of the Lower Burdekin floodplain. The project is titled "Development of a Lower Burdekin Numerical Groundwater Flow and Solute Transport Model". The project was managed by the Queensland Hydrology Unit of the Environment and Resource Sciences section of the Department.

Prior to completion of the project, the Queensland Hydrology Unit became part of the newly formed Department of Science, Information Technology, Innovation and the Arts (DSITIA). Where relevant, all previous references to DERM have been changed to DSITIA.

This report is part of a series of eleven technical reports produced for the project. The overarching title of all departmentally-produced reports is "Development of a hydrological modelling toolkit to support sustainable development of the Lower Burdekin groundwater system." The full list of reports produced for this project are:

1. Review of modelling methods
2. Conceptualisation of the Lower Burdekin aquifer
3. Groundwater flow modelling of the Lower Burdekin aquifer
4. Instructional solute transport model of the Lower Burdekin aquifer
5. A re-evaluation of groundwater discharge from the Burdekin floodplain aquifers using geochemical tracers
6. Quantification of evapotranspiration in a groundwater dependent ecosystem
7. Geochemical assessment and reactive transport modelling of nitrogen dynamics in the Lower Burdekin coastal plain aquifer
8. Predictive uncertainty of the Lower Burdekin groundwater flow model
9. MODFLOW local grid refinement for the Lower Burdekin aquifer
10. Hydroecology of the Lower Burdekin River alluvial aquifer and associated groundwater dependent ecosystems
11. Pesticides in groundwater in the Lower Burdekin floodplain

All reports were produced by DSITIA, with the exception of:

- Report #5 which was authored by the National Centre for Groundwater Research and Training, Flinders University, Adelaide; and
- Reports #10 and #11 which were completed in March 2012 as DERM reports.

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Executive Summary

The Lower Burdekin floodplain drains one of Australia's largest floodplain and delta environments (~ 1,250 km^2). The region supports one of Australia's most intensively cultivated and productive agricultural areas, with over 120,000 ha of irrigated crops, dominated (~100,000 ha) by sugarcane. The region represents Australia's largest single sugar producing environment, yielding approximately thirty percent of Australia's total sugar production. Pesticide use in sugar cane in the Lower Burdekin floodplain has previously been estimated as 98,000 kg a.i. $year^{-1}$ of herbicides, 538 kg a.i. $year^{-1}$ of insecticides and 716 kg a.i. $year^{-1}$ of fungacides (Simpson et al. 2001). Off site transport of these pesticides used in cropping in the Lower Burdekin floodplain poses a potential threat in terms of:

- contamination of the groundwater, affecting its use for domestic and townwater supplies and (to a lesser extent) irrigation water supply
- discharge to the environment, including streams, wetlands and directly into the Great Barrier Reef lagoon.

The objective of the current study was to provide measurements of pesticide concentrations approaching groundwater discharge zones in the Lower Burdekin floodplain. This information is intended to assist in the development of groundwater transport modelling for pesticides in this region which will facilitate prediction of the loads of pesticides entering the Great Barrier Reef sourced from groundwater.

Samples for pesticides were collected in August 2011 from 53 groundwater monitoring bores, and two surface stream sites, in the lower Burdekin floodplain. Sixteen bores were located in potential Riverine groundwater discharge zones and 37 in subterranean groundwater discharge zones. Water samples were chemically analysed by a NATA accredited laboratory for 142 pesticides including herbicides, insecticides and several fungicides.

Pesticides were present at detectable levels in 38% of groundwater samples taken from bores in the Burdekin River delta and Burdekin River Irrigation Areas. Four herbicides (atrazine, diuron, hexazinone and metolachlor) and two breakdown products of the herbicide atrazine (desethyl atrazine, desisopropyl atrazine) were detected in at least one of the 53 groundwater samples. The organophosphate insecticide, chlorpyrifos was detected in two of the groundwater bores sampled. The breakdown products of atrazine were the most commonly detected compounds (desethyl atrazine, N = 17, 32%; desisopropyl atrazine, N = 11, 21%), followed by atrazine itself (7, 13%). Other herbicides detected included hexazinone which was present above limits of detection in 4 samples (7.5%), while diuron was detected in 2 samples (3.8%), and metolachlor in one sample (1.9%). Atrazine and its breakdown products were not detected in samples from below 40 m (top of screen) and only once between 25 to 40 m. Similarly, diuron, hexazinone and metolachlor were not detected in samples from below 25 m screen depth. This is consistent with the long travel time presumably required for diffuse recharge to reach deeper aquifer layers.

None of the pesticide concentrations detected in groundwater exceeded human health guidelines for drinking water (NHMRC, 2011). Levels of the insecticide chlorpyrifos were above ecosystem health guideline concentrations (ANZECC, 2000) and so have potential to lead to contamination of freshwater ecosystems. According to indices of the potential for pesticides to leach to groundwater based on physical chemical properties (soil half lives and sorption coefficient) chlorpyrifos is considered to be a non-leaching compound. The detection of this highly sorbed pesticide in groundwater highlights the need for further research into understanding and predicting pesticide transport mechanisms to groundwater such as `preferential-flow' which have been demonstrated under field conditions.

It should be noted that the current study represents a one off sampling event and will not represent the range of concentrations present in groundwater of the Lower Burdekin over time. Given the regular use of groundwater in this region as a drinking water source and the proximity of this region to the World Heritage Listed Great Barrier Reef, it is recommended that this sampling be conducted on a regular basis at selected bores to track the concentrations of pesticides through the year relative to times of pesticide application. Further, ongoing sampling across multiple years would be required to provide insights into long term trends in pesticide concentrations in Lower Burdekin groundwater.

Introduction

The Lower Burdekin floodplain drains one of Australia's largest floodplain and delta environments (~ 1,250 km^2). The region supports one of Australia's most intensively cultivated and productive agricultural areas, with over 120,000 ha of irrigated crops, dominated (~100,000 ha) by sugarcane. The region represents Australia's largest single sugar producing environment, yielding approximately thirty percent of Australia's total sugar production. The remaining area is planted to mango plantations, cotton and mixed horticulture.

Pesticides (including herbicides, insecticides and fungicides) represent an integral component of farm management in the Queensland's cropping industries. While there are no recent estimates of the usage rates of pesticides in Queensland, reported usage from the sugar cane industry in 2000 is presented in Table 1. Off site transport of these pesticides following application in the Lower Burdekin floodplain poses a concern in terms of:

- contamination of the groundwater, affecting its use for domestic and townwater supplies and (to a lesser extent) irrigation water supply, and tailwater runoff
- discharge to the environment, including streams, wetlands and directly into the Great Barrier Reef lagoon.

Herbicides applied in cropping are regularly detected in surface water streams in the Burdekin catchment (Lewis et al. 2009; Davies et al. 2011; Smith et al. 2011) and have been detected in the World Heritage Listed Great Barrier Reef Marine Park off shore from the Burdekin catchment (Lewis et al. 2009, 2011; Shaw et al. 2010). In particular, herbicides that inhibit functioning of photosynthesis at photosystem II in plants (PSII herbicides; ametryn, atrazine, diuron, hexazinone, tebuthiuron) have been identified as a concern due to the frequency and concentrations of detections as well as potential ecotoxicological effects (Jones 2005, Harrington et al. 2005, Haynes et al. 2000, Lewis et al. 2011).

An alternative pathway to transport via surface waters for contaminants into the ocean and to streams is through groundwater discharge (Cook et al. 2011). The volume of groundwater inflow into the GBR lagoon by this pathway is much less certain than that moving as streamflow. Estimates of the groundwater discharge across the entire alluvial floodplain of the lower Burdekin are in the range of 30 – 150 GL yr^{-1} to surface water and 50 – 400 GL yr^{-1} to the ocean (Williams et al. 2008). In a more recent study, groundwater inflow over the 62 km of the Burdekin River downstream from Clare Weir[1] was estimated at 248,000 m^3 day^{-1} in May 2011 (Cook et al. 2011). In the Haughton River, 30 – 50 km upstream from the mouth, groundwater inflow was estimated as ~138,000 m^3 day^{-1}. Groundwater inflow for the 60 km reach above the mouth for Barratta Creek was estimated at 55,900 m^3 day^{-1}. The total groundwater flow to the three streams is 319,400 m^3 day^{-1} or 117 GL yr^{-1}. Total groundwater flow to the ocean (Bowling Green Bay) was 1,296,000 m^3 day^{-1} or 473 GL yr^{-1}. These estimates are similar to the higher end of the range of estimates given by Williams et al. (2008). These estimates represent one point in time and would vary seasonally and over time depending on groundwater levels in the Lower Burdekin aquifers. For comparison, annual discharge from the Burdekin River for the period 1922 to 2005 has been given as 8430 GL yr^{-1} (Lewis et al. 2006). Given these estimates, low concentrations of pesticides present in groundwater could potentially result in the load of pesticides being transported to the Great Barrier Reef through groundwater being significant in comparison to the surface water contribution.

Under the Reef Water Quality Protection Plan 2009 (Reef Plan), a target has been set to reduce the total transport of pesticides to the Great Barrier Reef by 50% by 2013. To report on progress towards this target, the Paddock to Reef program has been implemented as an integrated modelling, monitoring and reporting program (The Paddock to Reef Integrated Monitoring, Modelling and Reporting Program). Currently, groundwater contributions to pesticide loads entering the Great Barrier Reef are not well represented in the Paddock to Reef program modelling assessments due to gaps in knowledge. The objective of the current study was to provide measurements of pesticide concentrations up-gradient of groundwater discharge zones in the Lower Burdekin floodplain. This information is intended to assist in the development of groundwater transport modelling for pesticides in this region which will facilitate prediction of the loads of pesticides entering the Great Barrier Reef through groundwater each year.

[1] The end-of-system gauging station used for calculating contaminant loads for the stream is some kilometres downstream of Clare weir.

Table 1. Estimates of the volumes (kg of active ingredient per year) of pesticides applied to sugarcane regions in Queensland from 2000 on a total area of approximately 436 000ha (Simpson et al. 2001).

	North (92000ha)	Herbert (56000ha)	Burdekin (71000ha)	Central (128000ha)	South (89000ha)	TOTALS (436000ha)
Herbicides						
Atrazine	107594	33804	46480	116011	27696	331585
Diuron	34264	16718	7884	108691	29889	197446
2,4-D	50260	28237	13168	41103	8789	141557
Glyphosate	10267	4388	10052	53830	7088	85625
Ametryn	8688	2208	11768	51113	2205	75982
Paraquat	12065	3476	3752	15345	8167	42805
Trifluralin	1600	96	3768	10276	5480	21220
Asulam	1271			4659	12725	18655
MSMA	3960			5017	1359	10336
Pendimethalin	976	2760	992	539	627	5894
Hexazinone	2054	704		2758	79	5595
Ioxynil	27			3328		3355
Fluroxypur	1308	560			29	1897
2,2-DPA			296	130		426
Dicamba	191				28	219
Metolachlor	22				26	48
Diquat					17	17
Bromacil		9				9
Picloram				3		3
Insecticides						
Chlorpyrifos	2563	3104	538	20967	24767	74491
Ethoprophos					4751	4751
Aldicarb					1582	1582
Heptachlor	1134					1134
Diazinon	28					28
Brodifacoum[a]	8	4	1			13
Fungicides						
MEMC	724	400	472	378	321	2300
Prochloraz	71	99	100	184	177	631
Propiconazole	29	19	114	149	41	352
Flusilazole	8	14	18	30	15	71

[a] rodenticide

Hazards and mitigating factors for pesticide transport in the Lower Burdekin floodplain

The hazards for pesticides in groundwater in the Lower Burdekin floodplain include:

- the shallow depths to groundwater
- high rates of drainage though soils
- recharge of groundwater with river water which contains pesticides from the upstream catchment (e.g. introducing compounds not used in the floodplain itself)
- large quantitities of pesticide use (Hamilton and Haydon 1996; Simpson et al. 2001), particularly herbicides
- only a small fraction of the amount used entering groundwater could create μg L^{-1} concentrations
- potential stability of some compounds under specific sets of conditions in the unsaturated zone or in groundwater (e.g. stable temperatures, certain pH values, low rates of biological activity, anaerobic conditions)
- preferential flow pathways in soil and unsaturated zone, if they occur (e.g. old root channels from cleared native vegetation).

These factors all indicate a high potential for contamination of the groundwater in the Lower Burdekin.

Mitigating factors for pesticides in groundwater in the Lower Burdekin floodplain include:

- rapid dissipation[2] of pesticides in cane trash and (to a lesser extent) in surface soil under a tropical climate (e.g. high temperatures can increase the rate of dissipation)
- sorption of pesticides to soils, thereby limiting potential for transport through drainage to groundwater
- dissipation and slow travel times during transport through the subsoil and unsaturated zone
- slow travel time of groundwater from recharge site to discharge sites[3]
- increased dissipation during travel approaching/through discharge zones due to changing bio-chemical conditions (as may occur for nitrate but less certain for pesticides).

Previous studies

Evidence for pesticides applied in agricultural practices reaching groundwater in coastal Queensland was found as early as the 1980s when Brodie et al (1984) detected heptachlor and lindane (γHCH) in bores in the Burdekin floodplain (most organochlorine pesticides have since been banned from use in Queensland). However, groundwater monitoring efforts for pesticides in Queensland have been limited. Data from the studies that have been conducted suggest that current levels of pesticides in groundwater are generally below relevant drinking water guideline levels with several exceptions. Studies conducted in Queensland and other tropical regions of Australia are described below and summarised in Table 2.

Lower Burdekin floodplain

Bauld (1996) sampled 11 bores at multiple depths in the Lower Burdekin floodplain unconfined aquifer on two occasions (end of dry season in 1992 and 1993). In that study, 42 samples were analysed for a broad spectrum of pesticides (covering 80 active ingredients). Fourty four percent of samples had positive detections of atrazine and 15% exceeded the 1994 NHMRC 'minimum detection limits'[4] for atrazine (0.5 μg L^{-1}). Concentrations were generally low (one half to three quarters of positive samples <0.1 μg L^{-1}). However, atrazine concentrations at one site were 1.45 μg L^{-1} and 1.3 μg L^{-1} in 1992 and 1993 respectively. These values are below both the Australian

[2] Dissipation may involve losses by volatilisation, degradation or transformation (chemical, biological or photochemical) and, for more mobile pesticides, leaching or diffusion deeper into the soil (Silburn 2003).

[3] A recharge area is where water from above ground (precipitation) is transmitted downward to an aquifer. Discharge areas are the locations at which groundwater leaves an aquifer and flows to the surface.

[4] The NHMRC limit of determination is a regulatory construct. Exceeding the limit of determination indicates that contamination of drinking water has occurred; it does not necessarily indicate a hazard to public health (NHMRC 1994) (Keating *et al.* 1996).

freshwater guidelines (13 µg L^{-1}) (ANZECC and ARMCANZ 2000) and the Australian drinking water health guidelines (20 µg L^{-1}) (NHMRC and NRMMC 2011). The atrazine degradation product deethylatrazine (DEA) was also detected in 65 % of samples. Other pesticides, including those detected by Brodie et al. (1984), such as the organochlorines γHCH and heptachlor, were not detected in 1992-93.

Klok and Ham (2004) sampled irrigation water being applied, water moving through the soil profile (deep drainage water) and the soil itself at six sites across the Burdekin delta. Irrigation water (pumped from groundwater sources; sampled at outlets of 'fluming') was analysed on three occasions over the 2002–2003 season. These samples were analysed for pesticides, including the active ingredients of the most commonly used pesticides in the Lower Burdekin floodplain (2-methyl-4-chlorophenoxyacetic acid (MCPA), 2,4-dichlorophenoxyacetic acid (2,4-D), diuron, atrazine, ametryn, chlorpyrifos, pendimethalin and hexazinone). The groundwater samples returned no quantifiable levels of any pesticide.

Soils were analysed for pesticides in the 0.4–0.5, 0.9–1.0 and 1.4–1.5 m sections of the cores. There was a small amount (< 0.023 mg kg^{-1}) of diuron and atrazine in subsoils at a number of sites. These were detected at the 0.4–0.5 m and 0.9–1.0 m depths but not in 1.4-1.5 m depths. There were also small levels of pesticides moving though the soil profile in deep drainage water (Klok and Ham 2004). Atrazine was detected in four of the 67 drainage samples, diuron in 14 and 2,4-D detected in eight samples, with concentrations generally less than 1 µg L^{-1}.

Bundaberg

Hargreaves and Osbourne (pers. comm. 1996) analysed groundwater in the Budaberg region for organochlorine, organophosphate insecticides, phenoxy acid herbicides and carbamate pesticides. Pesticides were not detected in 49 of the 52 bores sampled. Traces of the herbicides 2,4-D, atrazine and the organophosphate insecticide chlorfenvinphos were detected in 3 bores, all at concentrations at or below 1.1 µg L^{-1} (Keating et al. 1996). These values are below both the Australian freshwater guidelines (280 and13 µg L^{-1} for 2,4-D and atrazine respectively (ANZECC and ARMCANZ 2000)) and the Australian drinking water health guidelines (30, 20 and 2 µg L^{-1} for 2,4-D, atrazine and chlorfenvinphos respectively (NHMRC and NRMMC 2011)).

Pioneer Valley

Baskaran et al. (2002) undertook sampling in the Lower Pioneer in April and May 1997 collected 46 groundwater samples. Shallow water tables are characteristic of the study area. Samples were analysed for physicochemical parameters (e.g. dissolved oxygen, pH, electrical conductivity (EC)), nutrients (e.g. dissolved organic carbon, nitrate, total dissolved phosphorus, orthophosphate), pesticides (154 compounds), trace metals, and contaminant and indigenous microbes. Thirty percent of groundwater samples were contaminated with one or more herbicides (ametryn, atrazine, deethylatrazine, bromacil, diuron and hexazinone), though none were present at concentrations exceeding relevant drinking water guideline values (NHMRC and NRMMC 2011). Diuron concentrations in four samples (1.8, 1.65, 0.47 and 0.24µg L^{-1}) exceeded the current Australian freshwater guidelines (0.2 µg L^{-1}) (ANZECC and ARMCANZ 2000). Detections were in the order diuron (9 samples, 20% of samples), deethylatrazine (7, 15%), atrazine (6, 14%), bromacil (4, 9%), ametryn (2, 4%), hexazinone (1, 2%). Although pesticide concentrations versus depth to water table showed no statistical relationship, 50% of pesticide positive samples were found in groundwater with depth to water table <5 m.

Masters (pers. comm. 2011) sampled one farm bore at Eton in 2008 for 14 LCMS herbicides (limit of reporting 0.01 µg L^{-1}) and detected atrazine (0.11 µg L^{-1}), desisopropyl atrazine (0.29 µg L^{-1}), desisopropyl atrazine (0.03µg L^{-1}), hexazinone (0.07 µg L^{-1}) and diuron (0.03 µg L^{-1}). These values are below relevant freshwater guidelines (13, 75 and 0.2 µg L^{-1} for atrazine, hexazinone and diuron respectively (ANZECC and ARMCANZ 2000)) and the Australian drinking water health guidelines (20, 40 and 20 µg L^{-1} for atrazine, hexazinone and diuron respectively (NHMRC and NRMMC 2011)).

Atherton and Southern Queensland

Samples of groundwater taken from bores in the Atherton Tablelands, Lockyer Valley and Darling Downs in Queensland in 1987 were analysed for the atrazine. Atrazine was not detected in any of the 28 groundwater samples analysed (limit of detection 0.1 µg L^{-1}) (Hunter 1992).

Southern Queensland

Silburn (pers. comm. 2011) sampled groundwater from three bores in the central Condamine alluvia in March 2009. Analyses were performed on these samples for 130 pesticides including organochlorines, organophosphates, triazine herbicides, phenoxyacid herbicides and synthetic pyrethroids. Concentrations were below limits of reporting for all compounds (0.01 μg L^{-1} for LCMS herbicides including atrazine and its breakdown products, 0.1 μg L^{-1} for phenoxyacid herbicides including 2,4-D).

Four bores were sampled in January 2011 and five bores in July to August 2011 in the Lockyer alluvia (Wolf, pers. comm. 2011). Samples collected in January 2011 were analysed for the same compounds (except without phenoxyacid screen) and the same reporting limits as for Silburn (pers. comm. 2011). Samples collected in July/August were analysed for 14 herbicides by LCMS with reporting limits of 0.005 μg L^{-1}. Bores were located near Glenmore Grove, Forest Hill, Tent Hill, Mulgowie and Gatton DEEDI research station. For samples collected in January 2011, all concentrations were below the limit of reporting except atrazine and metolachlor in one sample (0.04 and 0.03 μg L^{-1}) (Forest Hill, RN 14320806). Metolachlor was detected again in this bore in August 2011 (0.006 μg L^{-1}). These values are below the freshwater guideline (0.02 μg L^{-1}) (ANZECC and ARMCANZ 2000) and the Australian drinking water health guidelines (300 μg L^{-1}) (NHMRC and NRMMC 2011).

Ord River Irrigation Area (ORIA), Western Australia

Thirty groundwater monitoring bores located throughout the Ord River irrigation area were sampled on two separate occasions during June and November 2006 (Smith et al. 2007). A mixture of shallow and deep groundwater samples from the upper clay and silt aquifer and the basal sand and gravel aquifer, respectively, were collected. Analysis was conducted for 29 pesticides including acaracides, insecticides, rodenticides and namaticides (e.g. OC and OP compounds) and the herbicide atrazine. Of these 29 pesticides, only three were considered priority pesticides for the ORIA based on an inventory of pesticides used on the main crops grown in the area (atrazine, chlorpyrifos and endosulfan) (Oliver and Kookana 2005).

With the exception of atrazine, all pesticides tested for in this study were below their analytical detection limits in all groundwater samples. Atrazine was detected in six (10%) of the groundwater samples at concentrations less than 1 μg L^{-1}, which is below the relevant freshwater (13 μg L^{-1}) (ANZECC and ARMCANZ 2000) and Australian drinking water health guidelines (20 μg L^{-1}) (NHMRC and NRMMC 2011). It was present in three groundwater samples collected in June 2006 and in three samples from different monitoring bores collected in November 2006. These levels are significant but not currently recognised as a major concern to the environment or for drinking water use. Overall, the mean atrazine concentration in the groundwater samples containing atrazine was similar to the river and supply water mean concentrations. Sampling on two other occasions in the ORIA (2 bores each) also did not detect any compounds above the limits of detection.

Table 2. Summary of results from previous groundwater monitoring studies in Queensland

Region	Location	Timing	Pesticides analysed[a]	Pesticides detected	Detections/ Sample number	Levels detected (µg L^{-1})	Limit of Detection/ Reporting[b]	Comments	Reference
Burdekin floodplain	33 bores, 9 irrigation water, 4 water supplies	1976 - 1977	Organochlorines (γHCH, heptachlor)	γHCH, heptachlor	38/54	0–0.3	0.2 ng dm^{-1}	Sampling for very persistent organochlorine pesticides not currently in use.	Brodie et al. (1984)
Burdekin floodplain	11 bores	End of dry 1992 & 1993	Broad spectrum covering 80 pesticides	atrazine, deethylatrazine (DEA)	44% of 42 (atrazine), 65% of 42 (DEA)	0-1.45	NR	Other pesticides not detected.	Bauld et al. (1996)
Burdekin floodplain	Burdekin delta	2002, 2003	MCPA, 2,4-D, diuron, atrazine, ametryn, chlorpyrifos, pendimethalin, hexazinone	none	0/6	< 0.0001	0.0001 µg L^{-1}	Groundwater sampled from irrigation fluming. Atrazine, diuron and 2,4-D detected in deep drainage samples.	Klok and Ham (2004)
Western Australia	Ord River Irrigation Area	June/ Nov 2006	29 acaracides, insecticides, rodenticides, namaticides and atrazine	atrazine	6/30	< 1	0.1 µg L^{-1} (atrazine, OPs) 0.01 µg L^{-1} (OCs)	Analysis only included 3 of 25 'prioirty' pesticides for the ORIA (Oliver and Kookana, 2005)	Smith et al. (2007)
Burnett Mary	Bundaberg	Oct/ Nov 1993	LCMS, GCMS and phenoxyacid screen	atrazine, 2,4-D, chlorfenvinphos	3/52	<1.1	0.5 µg L^{-1} (atrazine) 0.1 µg L^{-1} (2,4-D)	All detections below NHMRC guidelines	Keating et al. (1996)
Mackay Whitsunday	Lower Pioneer	2002	Broad spectrum covering 154 pesticides	ametryn, atrazine, deethyl atrazine, bromacil, diuron, hexazinone	14/46	0.01-5.2	0.01 µg L^{-1}	All detections below drinking guidelines	Baskaran et al. (2002)
Mackay Whitsunday	Lower Pioneer (Eton)	2008	14 LCMS herbicides	atrazine, desisopropyl atrazine, diuron	1/1	0.1-0.12	0.01 µg L^{-1}		Masters (pers. comm. 2011)

Region	Location	Timing	Pesticides analysed[a]	Pesticides detected	Detections/ Sample number	Levels detected (µg L^{-1})	Limit of Detection/ Reporting[b]	Comments	Reference
Southeast Qld	Lockyer Valley	Jan-2011	14 LCMS, 114 GCMS screen	atrazine, metolachlor	1/4	0.03-0.04	0.01 µg L^{-1}		Wolf (pers comm. 2011)
Southeast Qld	Lockyer Valley	Jul-2011	14 LCMS, 114 GCMS screen	metolachlor	1/5	0.006	0.005 µg L^{-1} LCMS 0.1 µg L^{-1} GCMS		Wolf (pers comm. 2011)
Southwest Qld	Condamine	2009	130, LCMS, GCMS and phenoxyacid screen	none	0/3	< limits	0.01 µg L^{-1} LCMS, 0.1 µg L^{-1} GCMS		Silburn (pers comm. 2011)

[a] Refer to Appendix B for compounds included in general LCMS, GCMS and phenoxyacid pesticides screens

[b] Limits of detection are the minimum concentration that can be demonstrated to be different from a blank concentration within a stated confidence limit. The limit of detection is calculated for each analysis and varies depending on the sample matrix. Limits of reporting are set by a laboratory and are greater than the limit of detection as they include a safety factor to account for variability between samples. The limits listed in this table include both limits of detection and limits of reporting depending on the details included in the relevant reference.

NR=not reported; OCs=organochlorine pesticides; OPs= organophosphate pesticides.

Methods

Study location

The study was carried out on the coastal floodplain of the lower Burdekin, located south-east of Townsville in Queensland, Australia. This floodplain lies adjacent to the Great Barrier Reef World Heritage Area (GBRWHA). The area possesses a tropical climate characterised by hot wet summers (December to March) and dry winters (June to September). Average annual rainfall is 922 mm in Ayr and 574 mm at Clare (Figure 1) and average maximum temperatures are 29°C and 21°C respectively. The study region encompassed bores in the Burdekin River Delta, including both the North and South Burdekin Irrigation Areas (NBWB, SBWB), and the Burdekin Haughton Water Supply Scheme (BHWSS, also known as the Burdekin River Irrigation Area (BRIA)) (Figure 1). The BHWSS surface-water irrigation scheme was developed in the 1980's (Petheram et al. 2008) while the NBWB and SBWB have been in place since the 1960's (Bristow and Crough 2000).

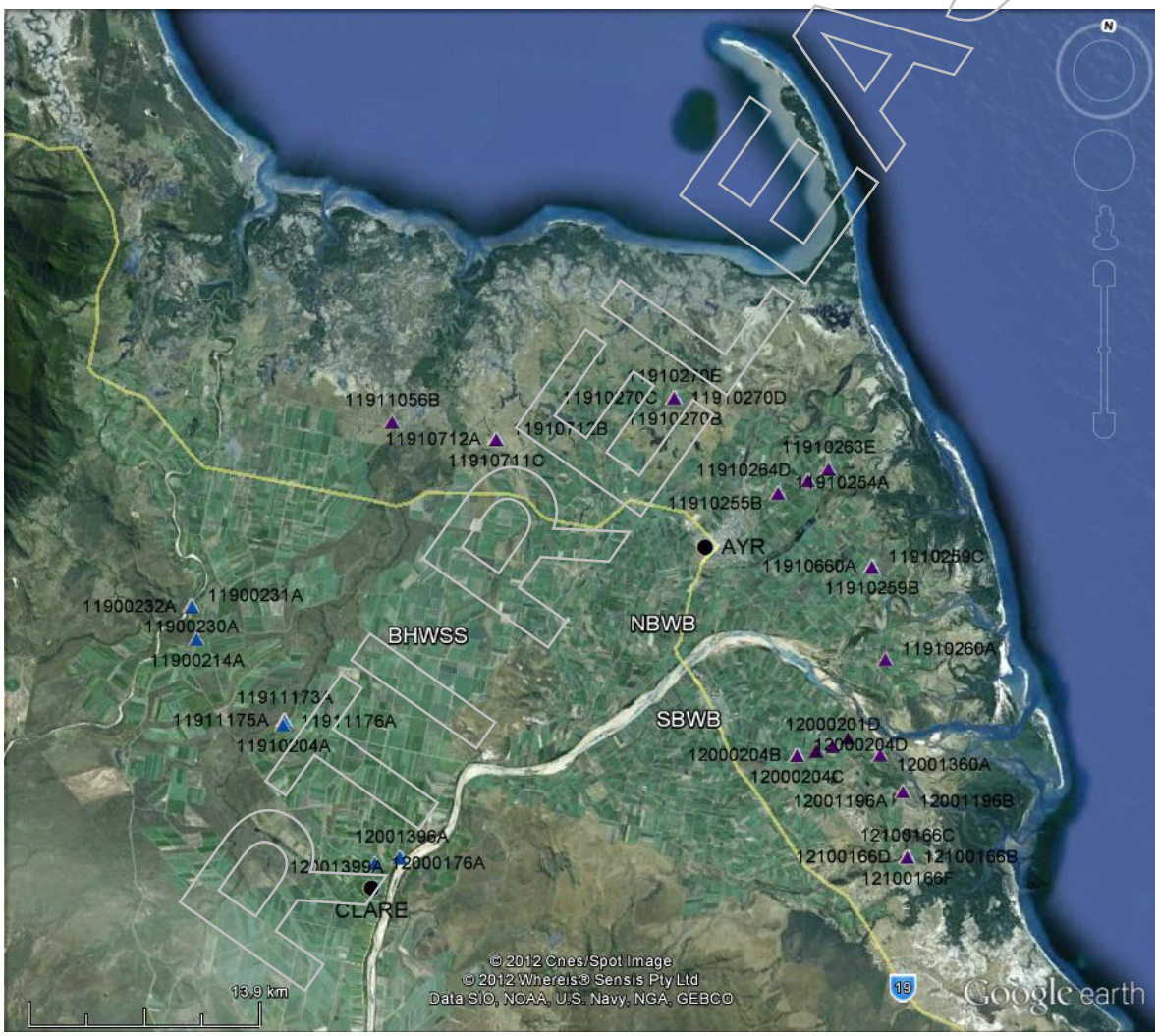

Figure 1. Location of groundwater bores sampled in the Lower Burdekin floodplain. Bores coloured purple are subterranean groundwater discharge sites while blue coloured bores are riverine groundwater discharge sites. BHWSS= Burdekin Haughton Water Supply Scheme (also known as the Burdekin River Irrigation Area (BRIA). NBWB=North Burdekin Water Board. SBWB=South Burdekin Water Board.

Bore selection and timing

This study was conducted as a one off sampling event with all bores sampled from the 16-28th August 2011. The rationale behind the locations selected for sampling is described in an accompanying report (Lenahan et al. 2012). The intention was to establish the geochemical conditions approaching groundwater discharge zones (Figure 1). A list of all bores sampled is provided in Appendix A. Nested piezometer sites located within the subterranean estuary were targeted to characterise the geochemical conditions that contaminants, if present, needed to flow though prior to discharging directly into the marine environment (including tidal creeks/wetlands, lagoons etc). The other sites were selected to characterise the geochemical conditions up-gradient of terrestrial discharge sites (riverine). These were the new piezometers installed as riparian zone transects at Haughton Powerline, Barratta Northcote, and Burdekin Clare river gauge sites. The closest existing piezometer located up-gradient of the transects was also sampled (e.g. 11900213 and 11900214 at Haughton; 11910204 at Barratta; 12000176 at Burdekin). Two surface water samples were also collected; from Barratta Creek at Northcote Gauge (119101A) and from the Burdekin River at the Clare gauge (120006A).

These sampling locations provide pesticides samples related to potential groundwater discharge. Sampling from transects towards and through the discharge zones provide some evidence about changes in pesticide concentrations in these zones, which relate to pesticide dissipation. Thus the spatial distribution of bores sampled is different to the locations that might be selected for sampling the occurrence of pesticides in the lower Burdekin aquifer systems for other purposes (e.g. Bauld 1996; Baskaran et al. 2002).

Sample collection

Samples were collected in accordance with water AS/NZS 5667.11:1998-Australian/New Zealand Standard Water quality-Sampling Part 11: 'Guidance on sampling of groundwaters'. Details of bore sampling protocols are provided in an accompanying report (Lenahan et al. 2012). Piezometers were purged three volumes and then sampled after electrical conductivity, dissolved oxygen, Eh (redox state), pH and temperature had stabilised using a piston driven Bennet™ (model 180) groundwater sampling pump. Three litres of water was collected in solvent rinsed amber glass bottles. Samples were stored on ice (<4^{o}C) in eskies in the field and transferred to refrigerated storage each day. The samples were shipped via refrigerated transport to the Queensland Health Forensic and Scientific Services (QHFSS) laboratory within 30 days of collection.

Sample extraction and analysis

Sample extraction and analysis was conducted by the QHFSS organics laboratory, which is accredited through the National Association of Testing Authorities. Selected compounds for which samples were analysed are listed in Table 3 with selected physical chemical properties. The full list of compounds included in the analysis is provided in Appendix B. Analysis was initiated the day following sample reciept at the laboratory.

Water soluble herbicides (QHFSS method number QIS29937) and phenoxyacid herbicides (QHFSS method number QIS 16631) were extracted through solid phase extraction cartridges and were analysed by LCMS and GCMS respectively. Organochlorine, organophosphate, synthetic pyrethroid and other herbicides (QHFSS method number QIS 16315) were solvent extracted followed by GCMS analysis. It should be noted that results from the solid phase extraction method will not include pesticides present in the sample sorbed to sediments, while the solvent extraction approach approach employed for the GCMS analysis will.

Table 3. Selected properties of compounds analysed taken from the footprint pesticides properties database (University of Hertfordshire, 2011). Only five of the 114 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.

Analyte	Soil Half lives	Soil sorption Coefficient (Koc)	Log K_{ow}	GUS leaching potential Index[b]
Herbicides by LCMS				
Ametryn	37	316	2.98	2.35
Atrazine	29	100	2.7	3.3
Bromacil	60 [a]	32	1.88	3.44
Diuron	89	1067	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	2432	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]	2600	3.8	0.67
2,4,5-T	350 [a]	-	4.0	-
Total Haloxyfop	9 [a]	75	-	2.03
Pesticides by GCMS				
Metribuzin	19	-	1.65	2.57
Pendimenthalin	90	17581	5.2	-0.39
Diazinon	18.4	609	3.69	1.14
Chlorpyrifos	21	8151	4.7	0.15
Propiconazole	214	1221	3.72	1.51

[a] Typical value instead of field value

[b] Calculated from the soil half life and partition coefficient. GUS = log t1/2 x (4 – log Koc) where Koc is the soil sorption coefficient (mL g^{-1}) and t1/2 is the half-life in soil (days). Higher values indicate greater potential for leaching. 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).

Results and Discussion

Occurrence of pesticides

Herbicides were detected in surface water samples collected from Barratta Creek and from the Burdekin River. Two herbicides, atrazine and metolachlor, were detected at concentrations of 0.006 and 0.007 ug L^{-1} respectively in the Burdekin River. Nine herbicides were detected (ametryn, atrazine, diuron, hexazinone, metolachlor, imidacloprid, MCPA, 2,4-D and metribuzin) in the Barratta Creek surface water sample. In addition, two breakdown products of the herbicide atrazine were detected in Barratta Creek (desethylatrazine, desisopropyl atrazine). Results for surface water samples collected from Barratta Creek and from the Burdekin River are summarised in Table 4.

Table 4. Results for Lower Burdekin surface water pesticide analysis, August 2011. Only pesticides which were detected in surface waters are listed.

Analyte	Freshwater Guideline Value (ANZECC[a])	Health Value (ADWG[b])	Public Health Regulation Standard[c]	Barratta Creek	Burdekin River
	2000	2011	2005	(µg L^{-1})	(µg L^{-1})
Herbicides by LCMS (Analytical limit of reporting = 0.005 µg L^{-1})					
Ametryn	-	70	50	0.01	
Atrazine	13	20	40	1.14	0.006
Desethyl Atrazine (DEA)	-	-	40	0.069	
Desisopropyl Atrazine	-	-	40	0.044	
Diuron	0.2	20	30	0.412	
Hexazinone	75	400	300	0.02	
Metolachlor	0.02	300	300	0.005	0.007
Imidacloprid	-	-	-	0.008	
Phenoxyacid Herbicides (Analytical limit of reporting = 0.1 µg L^{-1})					
MCPA	1.4	-	2	0.11	
2,4-D	280	30	30	0.13	
Other herbicides (Analytical limit of reporting = 0.1 µg L^{-1})					
Metribuzin	-	-	-	0.1	

[a] Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC and ARMCANZ 2000), trigger value for protection of 95% of species.

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

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

Herbicides and one insecticide were detected in groundwater from the lower Burdekin in August 2011. Four herbicides (atrazine, diuron, hexazinone and metolachlor) and two breakdown products of the herbicide atrazine (desethyl atrazine, desisopropyl atrazine) were detected in at least one of the 53 groundwater samples (Table 5). The organophosphate insecticide (chlorpyrifos) was detected in two of the groundwater bores sampled.

The breakdown products of atrazine were the most commonly detected compounds (desethyl atrazine, N = 17, 32%; desisopropyl atrazine, N = 11, 21%), followed by atrazine itself (7, 13%). Hexazinone was detected in 4 samples (7.5%), diuron was detected in 2 samples (3.8%), and metolachlor in one sample (1.9%).

Table 5. Results for Lower Burdekin groundwater pesticide analysis, August 2011. Only pesticides which were detected in groundwater are listed.

Analyte	Freshwater Guideline Value (ANZECC[a])	Health Value (ADWG[b])	Public Health Regulation Standard[c]	Percent detections (53 samples)	Concentration (µg L^{-1})	
	2000	2011	2005		Max	Mean
Herbicides by LCMS (Analytical limit of reporting = 0.005 µg L^{-1})						
Atrazine	13	20	40	13.2	0.031	0.019
Desethyl Atrazine (DEA)	-	-	40	32.1	0.254	0.070
Desisopropyl Atrazine	-	-	40	20.8	0.044	0.021
Diuron	0.2	20	30	3.8	0.125	0.072
Hexazinone	75	400	300	7.5	0.030	0.019
Metolachlor	0.02	300	300	1.9	0.009	0.009
Organophosphate insecticides (Analytical limit of reporting = 0.1 µg L^{-1})						
Chlorpyrifos	0.01	10	10	3.8	0.4	0.3

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

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

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

To provide an indication of how frequently pesticides were detected together in the same samples, concentrations were plotted against the concentrations of the most commonly detected pesticide, desethyl atrazine (N = 17, 32.1%) (Figure 2). From this graph it can be seen that metolachlor and diuron were not commonly detected. In comparison, atrazine and desisopropyl atrazine were commonly found in the same samples as desethyl atrazine due to application and subsequent breakdown of atrazine. All samples in which herbicides were detected also contained detectable levels of desethyl atrazine, with two exceptions. Atrazine, diuron and hexazinone alone were detected in the sample from bore 11191173A and diuron alone was detected in the sample from bore 12000204B.

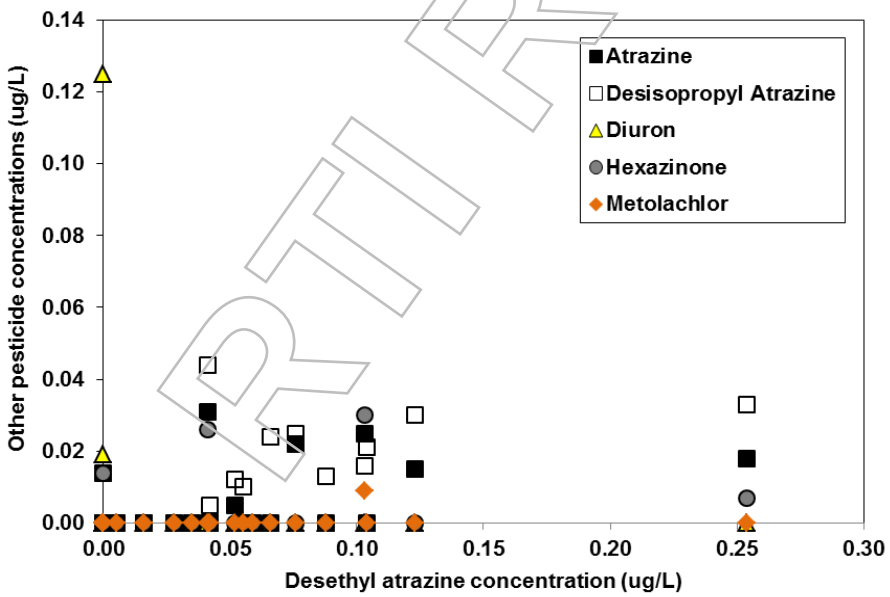

Figure 2. Concentrations of herbicides against that of desethyl atrazine, the most commonly detected compound.

Each of the pesticide active ingredients detected is registered for application in sugarcane cropping. It should be noted, however, that diuron use has been restricted by the Australian Pesticides and Veterinary Medicines Authority since this study was conducted. All of the bores sampled were in sugarcane growing areas. Atrazine and the atrazine degradation products were detected in bores in the BHWSS around Clare and in the SBWB around Home Hill (Figure 3). By contrast, these herbicides were not detected in bores sampled in the NBWB area around Ayr. Soils in the delta region (North and South Burdekin Water Board Areas) are typically more permeable than the friable clays in the BHWSS, which would indicate greater potential for pesticide transport to groundwater in the delta region. However, irrigation practices in the BHWSS were estimated to contribute to 160 GL yr^{-1} of deep drainage in the BHWSS in 2008, in contrast to natural deep drainage of around 15 GL yr^{-1} (Williams et al., 2008). Based on estimates of groundwater discharge to surface waters across the lower Burdekin alluvial floodplain, Williams et al (2008) theorised that the delta area may be acting as a drainage system for the groundwater of the BHWSS. The high rates of deep drainage in the BHWSS area are likely to explain the greater incidence of pesticide detections in this region. However, as this sampling represents one point in time, repeated sampling would be required to determine whether the observed spatial distribution of pesticides is consistent through time or rather if they are related to recent pesticide applications.

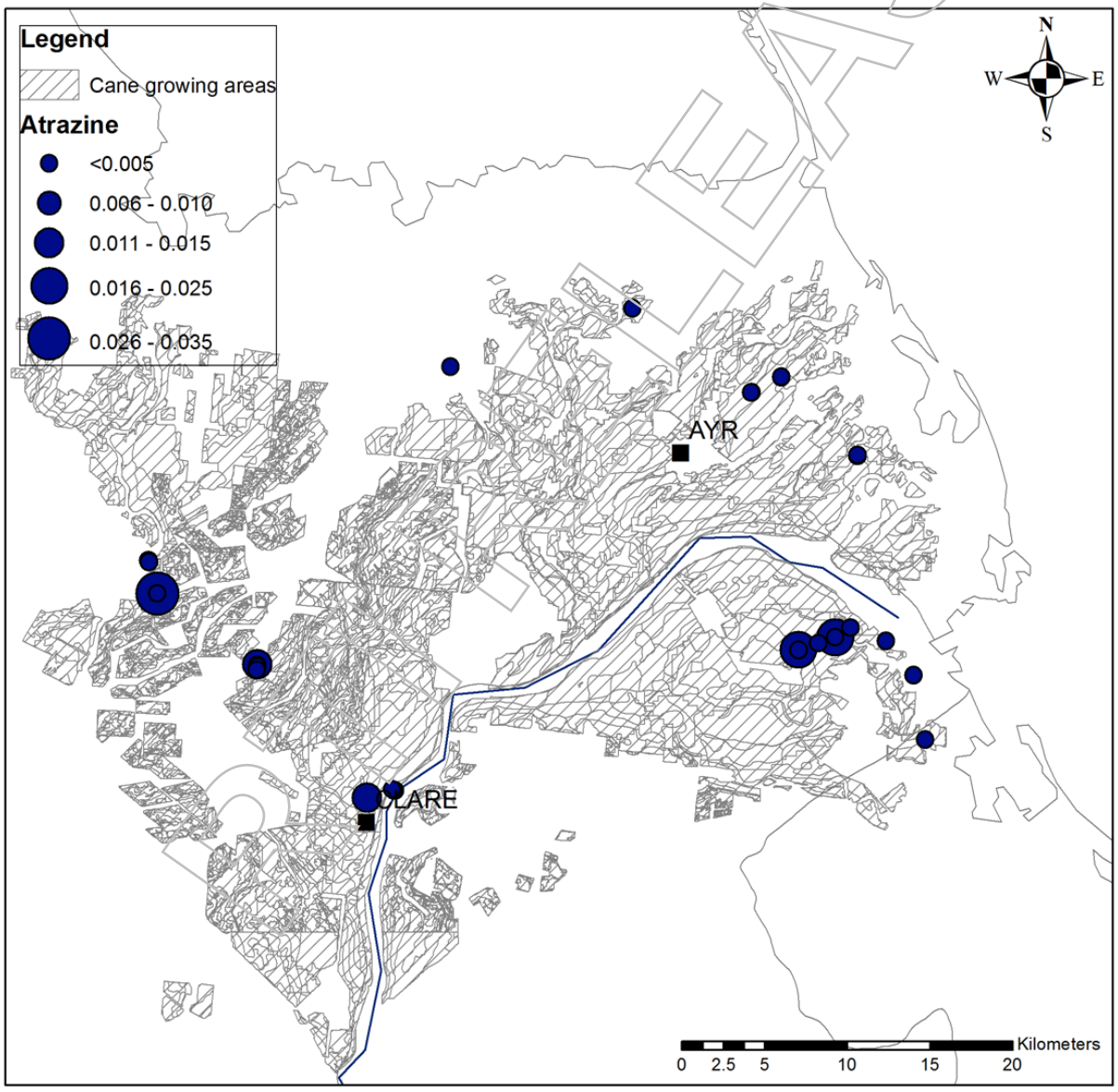

Figure 3. Concentrations of atrazine detected at bores sampled in the Lower Burdekin floodplain.

Atrazine and its breakdown products were not detected in samples from below 40 m (top of screen) and only once between 25 to 40 m (Figure 4). Similarly, diuron, hexazinone and metolachlor were not detected in samples from below 25 m screen depth (Figure 5). This is consistent with the long travel time presumably required for diffuse recharge to reach deeper aquifer layers.

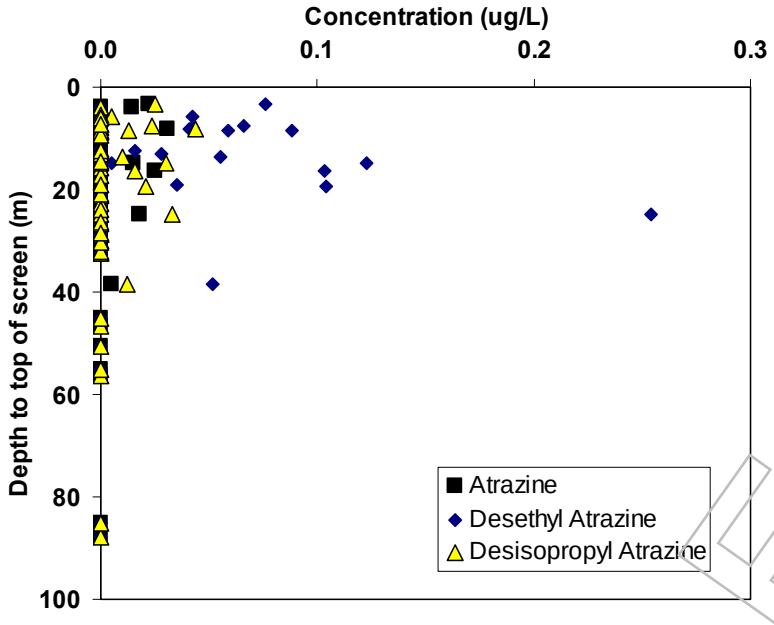

Figure 4. Concentrations of atrazine and its breakdown products against depth of the top of screen (below casing). Concentrations below the LOR are plotted as 0.0 to show all sampled depths.

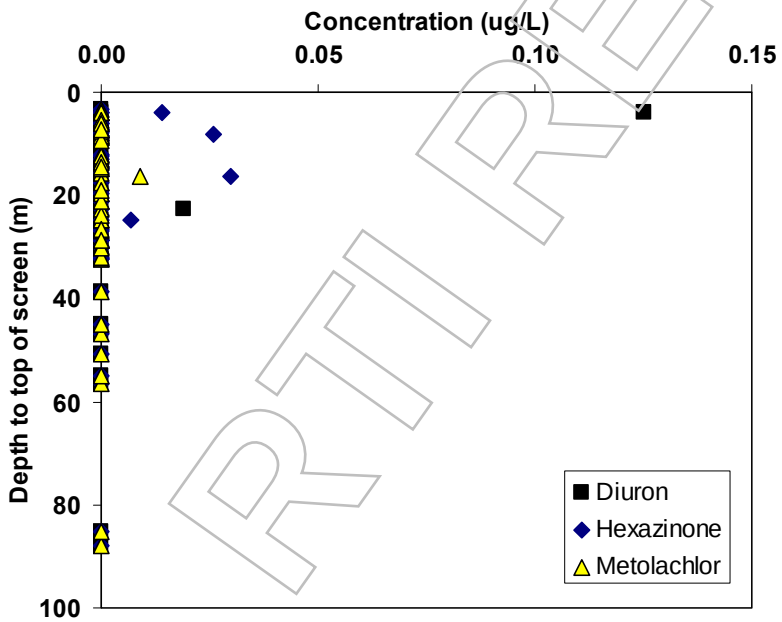

Figure 5. Concentrations of three herbicides against depth of the top of screen (below casing). Concentrations below the LOR are plotted as 0.0 to show all sampled depths.

Biodegradation of atrazine residues is expected to be slower in subsurface environments because microbial numbers and soil organic matter content decrease with depth. Therefore, degradation products of atrazine in groundwater are generally ascribed to leaching from the topsoil where most microbial activity takes place, rather

than in-situ degradation of atrazine (Rodriguez and Harkin, 1997). Prolonged soil atrazine residence times should result in large deethethylatrazine:atrazine ratio (DAR of >1). Conversely, DAR <1 values should occur when atrazine rapidly leaches (Baskaran et al., 2002). In the six samples from the current study in which a DAR could be calculated, the ratio was consistently >1 (1-14) indicating that transport to groundwater was not rapid. In the earlier Burdekin groundwater monitoring studies of Bauld (1996), the ratios of the parent compound:metabolites for atrazine indicated that rapid transport was occurring in some cases.

Of the compounds detected in surface water samples, only a subset were detected in groundwater. Generally, movement of pesticides is assumed to occur in the soil solution phase. Therefore, the pesticides of low aqueous solubility and relatively higher sorption are not expected to leach through the soil profile. The GUS leaching potential index which takes into account both soil half lives and partition coefficients, indicates that commonly applied herbicides such as atrazine, hexazinone and metolachlor have a high potential to be leached (values greater than 2.8) (Table 3). In agreement with the GUS leaching indices, atrazine is a commonly detected pesticide in groundwater monitoring studies worldwide (e.g. Stuart et al., 2012). However, this index is indicative only as the input properties (soil half lives and sorption coefficient) are likely to be different under varied field conditions and factors other than these properties may affect transport to groundwater.

Of the seven pesticides detected in groundwater, three had GUS leaching potentials greater than 2.8 (Table 3). However, two of the compounds detected had GUS leaching potential indices around or below 1.8 (diuron and chlorpyrifos). According to the GUS indices, these pesticides are highly unlikely to be detected in groundwater. However, in some field studies it has been observed that even the strongly sorbed pesticides can move preferentially along flow pathways, such that their travel times are comparable with conservative solutes (Flury 1994). Chlorpyrifos is commonly applied directly to the plant cane sett, cuttings of mature sugarcane stalks used as seed pieces, at planting and then immediately buried. This application method will reduce potential for rapid degradation and is likely to increase the potential for the pesticide to leach. Nevertheless, the detection of such a highly sorbed pesticide indicates the need to better understand and predict pesticide transport through leaching and potential for groundwater contamination.

Human health implications

The concentrations of the pesticides detected were consistently below Australian drinking water guideline values (NHMRC, 2011). The concentrations of chlorpyrifos measured ranged from 0.2-0.4 µg L^{-1}, and the maximum concentration detected is 25 times lower than the drinking water guideline value (10 µg L^{-1}). The health-based guideline values are derived from the acceptable daily intake (ADI) and are set at about 10 per cent of the ADI for an adult weight of 70 kg and a daily water consumption of 2 litres (NHMRC, 2011). These guideline values are relatively conservative. However, the presence of pesticides in drinking water supplies is a concern and indicates that ongoing monitoring is required.

Environmental implications

Concentrations of pesticides detected were generally below both freshwater ecosystem guidelines (ANZECC and ARMCANZ, 2000) and irrigation water quality guidelines for crop damage (ANZECC and ARMCANZ, 2000). The one exception to this was the organophosphate insecticide chlorpyrifos which was detected in two bores at concentrations (0.3, 0.4 µg L^{-1}) above the freshwater ecosystem health guideline values for protection of 95% (0.01 µg L^{-1}) of species. Although these guidelines are not intended for direct application to groundwaters, the fact that these concentrations were detected in discharge zones indicates potential for exposure of freshwater ecosystems to these levels of pesticides. There are currently no guidelines relevant to the protection of groundwater dependent ecosystems.

Estimates of the groundwater discharge across the entire alluvial floodplain of the lower Burdekin are in the range of 30 – 150 GL/yr to surface water and 50 – 400 GL/yr to the ocean (Williams et al. 2008). To place the potential contribution of groundwater to pesticide loads entering the Great Barrier Reef in context, these flows could carry loads of 30 - 150 kg (to surface water) and 50 - 400 kg (to the ocean) of a contaminant for each 1 µg L^{-1} concentration, compared to a total average annual load to the ocean in Burdekin region streamflow of combined PSII herbicides of 4,911 kg (Kroon et al. 2011). If flows are in the higher end of the ranges above and concentrations of combined PSII herbcides are several µg L^{-1} the total additional load to the GBR could become

significant. However, results from the current round of sampling indicate that concentrations of pesticides present are < 1 μg L^{-1}. Further sampling would be required to determine whether concentrations detected in the current sampling are representative of longer term average concentrations.

The comparison of a measured concentration to a guideline level is an approach commonly applied in risk assessments. However, it should be noted that this approach does not take into account the fact that organisms are not exposed to these pollutants in isolation but as one component of a complex mixture of pesticides and alongside other environmental stressors. Much more research is needed to demonstrate whether pesticides are or could potentially have an impact on groundwater dependent ecosystems and on the aquatic ecosystems to which the groundwater is discharged.

Gaps and future activities

The current sampling results provide a picture of the pesticide concentrations in groundwater discharge zones of the Lower Burdekin aquifers at one point in time. Further monitoring and field experimentation will be needed to develop an understanding of the potential for pesticide transport to groundwaters and the contribution of groundwaters as a source of pesticide loads entering the Great Barrier Reef lagoon.

Key research areas that require attention before risks of pesticides in groundwaters could be comprehensively assessed include:

- Improve tracking of pesticide use in agricultural and non-agricultural areas, including amounts, locations, and timing. Reliable information on usage is key to efficient and cost-effective water-quality monitoring and assessment, including development of predictive models.
- Evaluate potential effects of mixtures on humans and aquatic ecosystems. Mixtures are the most common mode of occurrence, but toxicity has not been assessed for many compounds and has been assessed only for a small proportion of specific combinations.
- Improve assessment of pesticide degradates. Although major degradates are considered as part of registration studies, environmental occurrence and potential adverse effects are not adequately understood.
- Improve methods for prediction of pesticide levels. There will never be enough resources to measure all the places, times, and compounds for which information is needed; thus, predictive tools are essential.
- Evaluate the effects of management practices on the transport of pesticides to groundwater.

Conclusions

Based on one off sampling of groundwater from 53 bores, pesticides were present at detectable levels in 38% of groundwater samples taken from bores in the Burdekin River delta and Burdekin River Irrigation Areas. Levels of the insecticide chlorpyrifos were above ecosystem health guideline concentrations and so have potential to lead to contamination of freshwater ecosystems. The detection of highly sorbed pesticides in groundwater highlights the need for further research into understanding and predicting pesticide transport mechanisms to groundwater such as 'preferential-flow' which have been demonstrated under field conditions.

Given the regular use of groundwater in this region as a drinking water source, linkages between ground and surface waters in this region, and its proximity to the World Heritage Listed Great Barrier Reef, it is recommended that this sampling be conducted on a regular basis at selected bores to track the concentrations of pesticides through the year relative to times of pesticide application.

References

ANZECC and ARMCANZ (2000). Australian and New Zealand guidelines for fresh and marine water quality / National Water Quality Management Strategy. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra.

Baskaran S, Budd KL, Rundi M. Larsen RM and Bauld J (2002). A Groundwater Quality Assessment of the Lower Pioneer Catchment, Qld. Bureau Of Rural Sciences Department Of Agriculture, Fisheries & Forestry, Canberra, Australia.

Bauld J (1996). Groundwater Quality: Human Impact on a Hidden Resource [online]. In: Hydrology and Water Resources Symposium (23rd : 1996 : Hobart, Tas.). Hydrology and Water Resources Symposium 1996: Water and the Environment; Preprints of Papers. Barton, ACT: Institution of Engineers, Australia, 1996: 143-147. National conference publication (Institution of Engineers, Australia); no. 96/05.

Bristow K and Crough J (2000). Managing the Burdekin aquifer. Australian Sugarcane. October-November,12-14.

Brodie JE, Hicks WS, Richards GN and Thomas FG (1984). Residues related to agricultural chemicals in the groundwaters of the Burdekin River Delta, North Queensland. Environmental Pollution (Series B) 8, 187-215.

Cook PG, Lamontagne S, Stieglitz T, Cranswick R, Hancock G and Shanafield M (2011). A re-evaluation of groundwater discharge from the Burdekin floodplain aquifer using geochemical tracers. NCGRT Technical Report. November 2011.

Davis AM, Thorburn PJ, Lewis SE, Bainbridge ZT, Attard SJ, Milla R, Brodie JE (2011). Environmental impacts of irrigated sugarcane production: Herbicide run-off dynamics from farms and associated drainage systems. Agric. Ecosys. Environ. Special Issue: Catchments and coral reef. In press. http://dx.doi.org/10.1016/j.agee.2011.06.019

Flury M, Fluhler H, Jury WA and Leuenberger J (1994). Susceptibility of soils to preferential flow of water: a field study. Water Resources Research, 30, 1945-1954.

Gustafson DI (1989). Groundwater ubiquity score: a simple method for assessing pesticide leachability. Environmental Toxicology and Chemistry 8, 339–357.

Hamilton DJ. and Haydon GF (1996). Pesticides and fertilisers in the Queensland sugar industry - estimates of usage and likely environmental fate. Dept of Primary Industries, Resource Management Institute, Meiers Rd, Indooroopilly, Queensland.

Harrington L, Fabricius K, Eaglesham G and Negri A (2005). Synergistic effects of diuron and sedimentation on photosynthesis and survival of crustose coralline algae. Mar. Pollut. Bull. 51, 415–427.

Haynes D, Ralph P, Prange J and Dennison B (2000). The impact of the herbicide diuron on photosynthesis in three species of tropical seagrass. Mar. Pollut. Bull. 41, 288–293.

Hunter HM (1992) Agricultural contaminants in aquatic environments: A review. Department of Primary Industries Qld, Brisbane. QB92002.

Jones R (2005). The ecotoxicological effects of photosystem II herbicides on corals. Mar. Pollut. Bull. 51, 495–506.

Keating BA, Bauld J, Hillier J, Ellis R, Weir KL, Sunners F and Connell D (1996). Leaching of nutrients and pesticides to Queensland groundwaters. pp. 151-163, In Hunter HM, Eyles AG, Rayment GR (Eds.), 'Downstream effects of land use'. Department of Natural Resources, Queensland, Australia.

Klok JA and Ham GJ (2004). A pilot study into pesticides and the Burdekin Delta aquifer system. Proc. Aust. Soc. Sugar Cane Technol., vol 26.

Kroon F, Kuhnert K, Henderson B, Henderson A, Turner R, Huggins R, Wilkinson S, Abbott B, Brodie J and Joo M (2010). Baseline pollutant loads to the Great Barrier Reef. CSIRO: Water for a Healthy Country Flagship Report series ISSN: 1835-095X. 41 pp.

Lenahan M (2012). Geochemical assessment and reactive transport modelling of nitrogen dynamics in the Lower Burdekin coastal plain aquifer. Townsville: Department of Science, Information Technology, Innovation and the Arts, Queensland Government.

Lewis SE, Brodie JE, Bainbridge ZT, Rohde KW, Davis AM, Masters BL, Maughan M, Devlin MJ, Mueller JF and Schaffelke B (2009). Herbicides: A new threat to the Great Barrier Reef. Environ. Pollut. 157, 2470–2484.

Lewis SE, Brodie JE, Ledee E and Alewijnse, M (2006). The spatial extent of delivery of terrestrial materials from the Burdekin Region in the Great Barrier Reef Lagoon. ACTFR report number 06/02. Australian Centre for Tropical Freshwater Research, James Cook University, Townsville.

Lewis SE, Schaffelke B, Shaw M, Brodie JE, Bainbridge ZT, Rohde KW, Kennedy KE, Davis AM, Masters BL, Devlin MJ and Mueller JF (2011). Assessing the additive risks of PS-II herbicide exposure to the Great Barrier Reef. Mar. Pollut. Bull.. Special Issue: Catchments and coral reef. In press. http://dx.doi.org/10.1016/j.marpolbul.2011.11.009

NHMRC and NRMMC (2011). Australian Drinking water Guidelines Paper 6 National Water Quality management Strategy. National Health and Medical Research Council, National Resource Management Ministerial Council, Commonwealth of Australia, Canberra.

Oliver D and Kookana R (2005). Pesticide use in the Ord River Irrigation Area, Western Australia, and risk assessment of off-site impact using Pesticide Impact Rating Index (PIRI). CSIRO Land and Water Technical Report 10/05, July 2005.

University of Hertfordshire (2011). Pesticides properties database. http://sitem.herts.ac.uk/aeru/footprint/en/index.htm

Petheram C, Bristow KL and Nelson PN (2008). Understanding and managing groundwater and salinity in a tropical conjunctive water use irrigation district Agric. Water Manag. 95, 1167-1179.

Reef Plan (2003). The State of Queensland and Commonwealth of Australia. Reef water quality protection plan; for catchments adjacent to the Great Barrier Reef World Heritage Area. Queensland Department of Premier and Cabinet, Brisbane, http://www.thepremier.qld.gov.au/library/pdf/rwqpp.pdf.

Reef Plan (2009). The State of Queensland and Commonwealth of Australia. Reef water quality protection plan; for catchments adjacent to the Great Barrier Reef World Heritage Area. Queensland Department of Premier and Cabinet, Brisbane, http://www.reefplan.qld.gov.au/library/pdf/reef-plan-2009.pdf.

Rodriguez CJ and Harkin JM (1997). Degradation of atrazine in subsoils, and groundwater mixed with aquifer sediments. Bulletin of Environmental Contamination and Toxicology. 59, 728-735.

Shaw MS, Furnas MJ, Fabricius K, Haynes D, Carter S, Eaglesham G and Mueller JF (2010). Monitoring pesticides in the Great Barrier Reef. Mar. Pollut. Bull. 60, 113-122.

Silburn M (2003) Characterising pesticide runoff from soil on cotton farms using a rainfall simulator. PhD Thesis, University of Sydney.

Simpson BW, Calcino D and Haydon G (2001). Pesticide and fertiliser use in the Australian sugar industry. Workshop Paper 3.2. In: Proceedings, Offsite movement of agrochemicals in tropical sugarcane production – extension workshop, Bundaberg, Australia, 8–9 May 2001. NR&M, ACIAR and MSIRI. Queensland Government, Department of Natural Resources & Mine, Brisbane.

Smith A, Pollock D, Palmer D and Price A (2007). Ord River Irrigation Area (ORIA) groundwater drainage and discharge evaluation: survey of groundwater quality 2006. CSIRO Land and Water Science Report 44/07, March 2007 (Rev. D)

Smith R, Middlebrook R, Turner R, Huggins R, Vardy S and Warne M (2011). Large-scale pesticide monitoring across Great Barrier Reef catchments – Paddock to Reef Integrated Monitoring, Modelling and Reporting Program. Mar. Poll. Bull. In press. doi:10.1016/j.marpolbul.2011.08.010

Stuart M, Lapworth D, Crane E and Hart A (2012). Review of risk from potential emerging contaminants in UK groundwter. Science of the Total Environment 416, 1-21.

Williams J, Stubbs T and Bristow KL (2008). A review of institutional arrangements in the Burdekin Irrigation Area with a view to managing sustainable farming practices in the region. Investigation Phase Report October 2008, Draft #13, 14/10/2008. John Williams Scientific Services Pty Ltd, Canberra ACT.

Appendix A

Table 5. Location and description of sampled bores in the Lower Burdekin floodplain.

Bore Name	Easting [a]	Northing	Standing Water Level (m)	Screen (m, top)	Screen (m, bottom)	Aquifer Charateristic	Purpose
11910255C	545987	7839063	4.08	12.4	14.4	Subterranean Estuary	Subterranean GW Discharge
11910263E	548842	7840809	1.94	24.9	26.9	Subterranean Estuary	Subterranean GW Discharge
11910263D	548842	7840809	2.54	39.6	41.6	Subterranean Estuary	Subterranean GW Discharge
11910263B	548842	7840809	3.19	75.5	77.5	Subterranean Estuary	Subterranean GW Discharge
11910263A	548842	7840809	3.24	86.5	88.5	Subterranean Estuary	Subterranean GW Discharge
12100166F	555821	7818158	1.78	7.2	9.2	Subterranean Estuary	Subterranean GW Discharge
12100166E	555821	7818158	2.16	15.8	17.8	Subterranean Estuary	Subterranean GW Discharge
12100166D	555821	7818158	2.41	21.2	23.2	Subterranean Estuary	Subterranean GW Discharge
12100166C	555821	7818158	2.5	26.8	28.8	Subterranean Estuary	Subterranean GW Discharge
12100166B	555821	7818158	12345	32.4	34.4	Subterranean Estuary	Subterranean GW Discharge
11910264D	547676	7839995	2.355	24.7	26.7	Subterranean Estuary	Subterranean GW Discharge
11910264C	547676	7839995	2.41	32.4	34.4	Subterranean Estuary	Subterranean GW Discharge
11910264B	547676	7839995	3.51	50.7	52.7	Subterranean Estuary	Subterranean GW Discharge
11910264A	547676	7839995	2.58	87.9	89.9	Subterranean Estuary	Subterranean GW Discharge
11911102A	547681	7840000	1.69	7.35	8.35	Subterranean Estuary	Subterranean GW Discharge
12000201D	550720	7824340	3.47	7.8	9.8	Subterranean Estuary	Subterranean GW Discharge
12000201C	550720	7824340	3.67	16.4	18.4	Subterranean Estuary	Subterranean GW Discharge
12000201B	550720	7824340	3.79	24.7	26.7	Subterranean Estuary	Subterranean GW Discharge
12000201A	550720	7824340	12345	38.6	40.6	Subterranean Estuary	Subterranean GW Discharge
12000202D	549744	7823957	3.655	5.9	7.9	Subterranean Estuary	Subterranean GW Discharge
12000204D	548629	7823588	1.23	3.4	5.4	Subterranean Estuary	Subterranean GW Discharge
12000204C	548629	7823588	0.96	13	15	Subterranean Estuary	Subterranean GW Discharge

Bore Name	Easting [a]	Northing	Standing Water Level (m)	Screen (m, top)	Screen (m, bottom)	Aquifer Charateristic	Purpose
12000204B	548629	7823588	0.95	19.5	21.5	Subterranean Estuary	Subterranean GW Discharge
12000204A	548629	7823588	12345	30	32	Subterranean Estuary	Subterranean GW Discharge
12000202C	549744	7823957	4	22.7	24.7	Subterranean Estuary	Subterranean GW Discharge
12000202B	549744	7823957	4.035	28.7	30.7	Subterranean Estuary	Subterranean GW Discharge
12000202A	549744	7823957	4.345	39.7	41.7	Subterranean Estuary	Subterranean GW Discharge
12001196B	555174	7822041	2.89	4	20	Subterranean Estuary	Subterranean GW Discharge
12001196A	555174	7822041	3.53	24	30	Subterranean Estuary	Subterranean GW Discharge
12001358A	551567	7824900	3.08	26.45	27.45	Subterranean Estuary	Subterranean GW Discharge
12001360A	553603	7824095	3.93	8.65	9.65	Subterranean Estuary	Subterranean GW Discharge
11910255B	545987	7839063	4.87	28.8	30.8	Subterranean Estuary	Subterranean GW Discharge
11910255A	545987	7839063	4.99	46.7	48.7	Subterranean Estuary	Subterranean GW Discharge
11910254A	545972	7839080	6.58	85.3	87.3	Subterranean Estuary	Subterranean GW Discharge
11910712B	528817	7840643	2.94	12	14	Subterranean Estuary	Subterranean GW Discharge
11910712A	528817	7840643	2.95	21	23	Subterranean Estuary	Subterranean GW Discharge
11910711C	528820	7840643	3.69	32	34	Subterranean Estuary	Subterranean GW Discharge
11910711B	528820	7840643	4.25	45	47	Subterranean Estuary	Subterranean GW Discharge
11910711A	528820	7840643	3.81	56.5	58.5	Subterranean Estuary	Subterranean GW Discharge
11910270E	539205	7844138	2.54	8.9	10.9	Subterranean Estuary	Subterranean GW Discharge
11910270D	539205	7844138	2.56	17.4	19.4	Subterranean Estuary	Subterranean GW Discharge
11910270C	539205	7844138	2.92	30.3	32.3	Subterranean Estuary	Subterranean GW Discharge
11910270B	539205	7844138	3.45	39.1	41.1	Subterranean Estuary	Subterranean GW Discharge
11910270A	539205	7844138	3.75	60.4	62.4	Subterranean Estuary	Subterranean GW Discharge
11911056B	522490	7841093	0.97	12.1	13.1	Subterranean Estuary	Subterranean GW Discharge
11900230A	511544	7829015	8.72	8.5	10.5	Floodplain - Riparian Zone_Haughton	Riverine GW Discharge

Bore Name	Easting [a]	Northing	Standing Water Level (m)	Screen (m, top)	Screen (m, bottom)	Aquifer Charateristic	Purpose
						Transect	
11900231A	511568	7828990	8.27	8.5	10.5	Floodplain - Riparian Zone_Haughton Transect	Riverine GW Discharge
11900232A	511597	7828939	7.99	7.5	9.5	Floodplain - Riparian Zone_Haughton Transect	Riverine GW Discharge
11900214A	512069	7827027	2.45	8.2	9.5	Floodplain_Haughton Transect	Riverine GW Discharge
11900213A	512069	7827029	2.28	19	21	Floodplain_Haughton Transect	Riverine GW Discharge
11911173A	517783	7822764	4.36	3.8	5.8	Floodplain - Riparian Zone_Barratta Transect	Riverine GW Discharge
11911174A	517788	7822736	12345	4	6	Floodplain - Riparian Zone_Barratta Transect	Riverine GW Discharge
11911175A	517786	7822698	4.13	5.5	7.5	Floodplain - Riparian Zone_Barratta Transect	Riverine GW Discharge
11911176A	517778	7822645	3.79	6	8	Floodplain - Riparian Zone_Barratta Transect	Riverine GW Discharge
11910204A	517733	7822436	3.46	12.5	13	Floodplain_Barratta Transect	Riverine GW Discharge
12001396A	525576	7815183	10.39	14.7	16.7	Floodplain - Riparian Zone_Burdekin Transect	Riverine GW Discharge
12001397A	525550	7815194	7.21	13.5	15.5	Floodplain - Riparian Zone_Burdekin Transect	Riverine GW Discharge
12001399A	525455	7815229	11.42	14.5	16.5	Floodplain - Riparian Zone_Burdekin Transect	Riverine GW Discharge
12000176A	524010	7814717	7.2	14.7	16.7	Floodplain_Burdekin Transect	Riverine GW Discharge
11910260A	553349	7829809	2.84	52.6	54.6	Subterranean Estuary	Subterranean GW Discharge
11910259C	552004	7835231	3.05	28.6	30.6	Subterranean Estuary	Subterranean GW Discharge
11910259B	552004	7835231	4.12	55.1	57.1	Subterranean Estuary	Subterranean GW Discharge
11910660A	552013	7835272	2.84	9.5	11	Subterranean Estuary	Subterranean GW Discharge

[a] Projected Coordinate System - GDA_1994_MGA_ Zone_55

Appendix B

Table 6. Herbicides included in QHFSS LCMS analysis.

Herbicides
Ametryn
Atrazine
Bromacil
Desethyl Atrazine
Desisopropyl Atrazine
Diuron
Fluometuron
Hexazinone
Metolachlor
Prometryn
Simazine
Tebuthiuron
Terbutryn
Imidacloprid

Table 7. Herbicides included in QHFSS phenoxyacid screen using GCMS.

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

Table 8. Pesticides included in the QHFSS broad screen using GCMS.

Organochlorine Pesticides
Aldrin
Chlordane cis
Chlordane Trans
Chlordene
Chlordene Epoxide
DDD (op)

Organochlorine Pesticides
DDD (pp)
DDE (op)
DDE (pp)
DDT (op)
DDT (pp)
Total DDT
Dicofol
Dieldrin
Endosulfan alpha
Endosulfan beta
Endosulfan Sulphate
Endosulfan Ether
Endosulfan Lactone
Total Endosulfan
Endrin
Endrin aldehyde
HCB
HCH alpha
HCH beta
HCH delta
Heptachlor
Heptachlor Epoxide
Lindane
Methoxychlor
Nonachlor trans
Oxychlordane
Organophosphorus Pesticides
Azinphos ethyl
Azinphos methyl
Bromophos ethyl
Cadusafos
Carbophenothion
Chlorfenvinphos
Chlorpyrifos
Chlorpyrifos methyl
Chlorpyrifos oxon
Coumaphos
Diazinon
Dichlorvos
Dimethoate
Ethion
Ethoprophos
Etrimphos

Organochlorine Pesticides
Famphur
Fenamiphos
Fenchlorphos
Fenitrothion
Fenthion ethyl
Fenthion methyl
Isophenphos
Malathion
Methidathion
Mevinphos
Parathion ethyl
Parathion methyl
Phorate
Phosmet
Pirimiphos methyl
Profenofos
Prothiophos
Pyrazophos
Tetrachlorvinphos
Terbufos
Herbicides (analysed by GCMS)
Bromacil
Diclofop methyl
Haloxyfop 2-etotyl
Haloxyfop methyl
Metolachlor
Metribuzin
Oxyfluorfen
Pendimethalin
Propanil
Propazine
Terbuthylazine
Terbutryn
Tri-allate
Trifluralin
Other Pesticides
Benalaxyl
Bitertinol
Carbaryl
Dichlorfluanid
Dichloran
Fipronil
Furalaxyl

Organochlorine Pesticides
Metalaxyl
Oxadiazinon
Piperonyl Butoxide
Pirimicarb
Procymidone
Propiconazole
Propoxur
Tebuconazole
Tetradifon
Vinclozolin
Synthetic Pyrethroids
Bifenthrin
lambda-Cyhalothrin
Cyfluthrin
Cypermethrin
Deltamethrin
Fluvalinate
Phenothrin
Tetramethrin
Transfluthrin
Permethrin
Fenvalerate
Allethrin
Bioresmethrin
Imazapic
Fluazuron