Department of Science, Information Technology, Innovation and the Arts

Pesticides and nutrients in groundwater and their transport to rivers from sugar cane cropping in the lower Burdekin

RP53C

Water Quality and Investigations

January 2015

Great state. Great opportunity.

Queensland Government

Prepared by

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Executive summary

Reef Plan is a joint initiative between the Queensland and Australian Governments which has a primary focus to address diffuse pollution from broadscale land use and to work with stakeholders to improve water quality reaching the Great Barrier Reef. The potential contribution of groundwater to the overall contaminants reaching the reef has been identified as a data gap in the understanding of pollutant pathways to the reef. In order to address this data gap, the Queensland Government provided support for this project under the Reef Water Quality Science Program.

The main aim of the project was to increase the understanding of the role of groundwater in transporting photosystem II inhibiting herbicides and nutrients to the reef, with a focus on the potential transport and transformation of contaminants through the riparian zone. Monthly sampling was undertaken between November 2011 and April 2013 at sites adjacent to the Haughton River, Barratta Creek, Burdekin River and adjacent to the Ramsar listed wetlands in Bowling Green Bay.

The concentration of nitrate and phosphate decreased through the riparian zone of Barratta Creek at Northcote and of Burdekin River at Clare, whilst the concentration of ammonium increased towards the river. Geochemical conditions measured at these sites indicated that nitrate may be being attenuated through the microbial process of denitrification. The increased ammonium concentrations towards the riverbanks were possibly a result of the decomposition of organic material within the riparian zone, rather than microbial transformation of nitrate. There was little change in the concentrations of nitrate and phosphate through the riparian zone at the Haughton River. The reason for this is not fully understood.

Concentrations of pesticides were present but were generally low in the groundwater at all sites, apart from the transect area of Barratta Creek at Northcote. This site showed a large temporal variation in pesticide concentration with peaks in concentrations following a flood event at the end of January 2013. This, along with a large decrease in specific conductivity following the flood event indicated that lateral exchange with the creeks surface water may be occurring. The pesticide concentrations decreased in these bores over a period of two months after the flood.

Groundwater loads were estimated at Barratta Creek at Northcote and Burdekin River at Clare. The overall contribution of groundwater to the loads of pesticides, nitrates and phosphate at these sites were low during the study period. However, the contribution of ammonia from groundwater to ammonia loads was significant.

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List of Abbreviations

Abbreviation	Definition
AHD	Australian Height Datum
BHWSS	Burdekin Haughton Water Supply Scheme
DAR	Desethylatrazine to atrazine ratio
DEA	Desethyl atrazine
DIA	Desisopropyl atrazine
DOC	Dissolved organic carbon
DNRA	Dissimilatory nitrate reduction to ammonium
DNRM	Department of Natural Resources and Mines
DSITIA	Department of Science, Information Technology, Innovation and the Arts
GBRCLMP	Great Barrier Reef Catchment Loads Monitoring Program
GWDB	Queensland Groundwater Database
MAR	Managed Aquifer Recharge
NATA	National Association of Testing Authorities
NBWB	North Burdekin Water Board
NWC	National Water Commission
LCMS	Liquid Chromatography – Mass Spectroscopy
LDPE	Low density polyethylene
LOR	Limit of reporting
ORP	Oxidation reduction potential
RN	Registered Number
P2R	Paddock to Reef
PSII pesticides	Photosystem II inhibiting pesticides
QHFSS	Queensland Health Forensic and Scientific Services
QWQGs	Queensland Water Quality Guidelines
SBWB	South Burdekin Water Board
SC	Specific conductivity
STE	Subterranean estuary
TV	Trigger value

1. Introduction.

Reef Plan is a joint initiative between the Queensland and Australian Governments, which has a primary focus to address diffuse pollution from broadscale land use and to work with stakeholders to improve water quality reaching the Great Barrier Reef (GBR). In order to prioritise and provide advice on management actions to improve Reef health and resilience, an understanding is needed of the mechanisms and pathways by which pollutants leave the land and are transported to the Reef. Considerable effort has been invested in understanding surface (stream and overland) transport of pollutants, most notably through the Paddock to Reef (P2R) monitoring and modelling program. However, much less is known about the subsurface transport of pollutants through the groundwater system, which may be important for both soluble nutrients and pesticides. The 2008 Scientific Consensus Statement (Brodie et al. 2008) on water quality in the GBR noted that "a high degree of uncertainty exists in the role of groundwater transported contaminants in material transport from paddocks to coastal waters". This situation had not significantly changed by the time the 2013 Scientific Consensus Statement (Brodie et al. 2013) was released. It stated that

> ‘The Wet Tropics, Burdekin and Mackay-Whitsundays catchments contribute over 85 per cent to the total photosystem inhibiting herbicides load to the Great Barrier Reef lagoon, with sugarcane being the main source (94 per cent). Groundwater may potentially be an important source of photosystem II inhibiting herbicides (as well as dissolved nutrients) to critical nearshore ecosystems of the Great Barrier Reef lagoon; however, insufficient information is currently available to evaluate the risks.‘

The Queensland Government provided support for a number of Research and Development projects under the Reef Water Quality Science Program (formerly the Reef Protection Program) in order to fill in knowledge gaps between agricultural practices and reef water quality. Specifically, the program was ‘tasked with reducing, through improved on-farm management, the off-farm transport to the Reef lagoon of contaminants from cane-growing areas in the Wet Tropics, lower Burdekin, and Mackay-Whitsunday areas’ (Hunter 2012, pg 1).

Hunter (2012) was funded to review the current knowledge of aquifers and groundwater processes in regards to photosystem II inhibiting (PSII) herbicides and nutrients. Shaw et al. (2012) followed with the development of a more refined method for measuring pesticides in groundwater and a one-off recognisance survey of the occurrence of pesticides in the discharge zones of the lower Burdekin. The current project was funded to monitor groundwater for pesticides, especially PSII pesticides and dissolved nutrients in areas associated with sugar cane cropping in the lower Burdekin with a focus on temporal trends through the riparian zone.

The main aims of the project were to:

1. Monitor groundwater contamination of PSII pesticides and dissolved nutrients associated with sugar cane cropping in the lower Burdekin
2. Improve temporal and spatial understanding of the movement of contaminants in groundwater through the riparian zone
3. Estimate the proportion of contaminants loads delivered by groundwater in the lower Burdekin catchment to the GBR and Ramsar wetlands
4. Assist in delivering Reef Plan targets by estimating the loads from ground and surface water and to assess the impact of overall paddock scale management practices over time.

2. Background to Project.

The lower Burdekin is made up of three main irrigation areas, the North Burdekin Water Board (NBWB), the South Burdekin Water Board (SBWB) (collectively locally known as the Burdekin River delta (SKM 2009)) and the Burdekin Haughton Water Supply Scheme (BHWSS). Sugarcane is the major crop in the lower Burdekin region, although cotton and horticultural crops such as mangoes, corn and rockmelon are also grown in small amounts (SKM 2009). The Burdekin River delta was developed in the 1860s and sugarcane was first grown in the region in 1879 (SKM 2009). Expansion of the sugarcane industry and excessive groundwater pumping in the area led to depletion of the groundwater (SKM 2009) and saltwater intrusion (Narayan et al. 2003; Petheram et al. 2008) and since the mid-1960s Managed Aquifer Recharge (MAR) has been occurring in the area. Groundwater is predominantly used for irrigation in the Delta region (80-90%) (SKM 2009). Conversely, the BHWSS was developed in the late 1980s with an emphasis on surface water irrigation, and in this area rising groundwater has been identified as a problem (Petheram et al. 2008). Approximately 80% of the irrigation in this area is from surface water (SKM 2009).

The average annual rainfall in the Lower Burdekin is around 1000 mm/year, but is highly variable, ranging from <200 to >1800 mm/year (Petheram et al. 2008). The area has wet summers (December to March) and dry winters (June to September) (Thayalkumaran et al. 2008). An unconfined aquifer system is present in the lower Burdekin region (Klok and Ham 2004). The BHWSS area tends to have finer deposits that the Burdekin River delta area and is likely to have occurred from deposition during overbank flow events (Petheram et al. 2008).

A number of groundwater studies have been undertaken in the Burdekin River delta area (Hunter 2012 and references therein), however fewer have been undertaken in the BHWSS area (Petheram et al. 2008). Overall, the concentration of nitrate in the groundwaters of the Burdekin appears to be increasing (Hunter 2012). Between 1992 and 1993 Bauld et al. (1996) found that 26% of samples had a nitrate-N concentration of >3 mg/L and 5% had a concentration of >10 mg/L in the Burdekin River delta. Hunter (2012) stated that the overall mean concentration of nitrate in the lower Burdekin region as 2.0 mg/L nitrate as N. This was based on data collected from 714 bores between 1990 and 2005 (data are available from the Queensland Groundwater Database (GWDB)). Hunter (2012) stated that overall the concentration of nitrate in the groundwater appears to be increasing.

Very few studies on pesticides in groundwater have been undertaken in the Burdekin region. In 1984, Brodie et al. (1984) detected heptachlor and lindane in bores in the delta area. Bauld et al. (1996) undertook a study in the Burdekin River delta at the end of the dry season in 1992 and in 1993, and measured 80 pesticides in 11 bores. Atrazine was detected in 44% of 42 samples. Its breakdown product, desethyl atrazine (DEA), was detected in 65% of samples, with a concentration range of not detected to 1.45 µg/L. Between 2002 and 2003, Klok and Ham (2004) collected three samples of irrigation water (sourced from groundwater) from each of six sites and analysed them for eight pesticides[1]. No pesticides were detected at concentrations greater than the limit of reporting (i.e. at a quantifiable level) in the groundwater, although atrazine, 2,4-D and chlorpyrifos were detected. They also measured pesticides in soil pore water and detected 2,4-D, atrazine and diuron.

Shaw et al. (2012) collected samples in 53 bores in the lower Burdekin in August 2011 and commonly detected atrazine and its breakdown products DEA and desisopropyl atrazine (DIA). Diuron, hexazinone, metolachlor and chlopyrifos were also detected. They found that the

[1] MCPA, 2,4-D, diuron, atrazine, ametryn, chlorpyriphos, pendimethalin and hexazinone

organophosphate insecticide chlopyrifos was present at concentrations above the ANZECC and ARMCANZ (2000) trigger value (TV) for ecosystem protection in two bores.

Hunter (2012) estimated groundwater as contributing approximately 28% to the overall nitrate loads and 12% of total dissolved phosphate loads to the GBR based on the mean concentration of these contaminants in groundwater in the Burdekin area. This does not take into account the potential of nitrate to transform via geochemical processes as it moves through riparian zone (see Lenahan 2012) nor the large approximations used to estimate the groundwater outflow.

3. Methodology

3.1. Sampling Sites and Sampling Frequency

The National Water Commission (NWC) funded a program that developed hydrogeological models for the Burdekin region (e.g. Foy and Bajracharya 2012; Lenahan 2012; McMahon et al. 2012; Reading et al. 2012; Wang et al. 2012) and installed a number of bores for monitoring purposes. The bores were situated along transects that crossed riparian areas of rivers adjacent to sugar cane fields. Three transects at three NWC sites were monitored as part of the current study (Figure 1). These sites were:

1. Haughton River at Powerline
2. Barratta Creek at Northcote
3. Burdekin River at Clare.

The transects were approximately 150 m in length and contained four piezometers (of which three were monitored). Additionally, an established bore in or on the edge of a field was sampled at each site. A fourth site, Barratta Creek at Jerona Road, which is situated on the edge of the Ramsar listed wetland Bowling Green Bay, was also sampled (Figure 1).

Physico-chemical parameters (i.e. pH, dissolved oxygen, specific conductivity (SC) and temperature) and samples for pesticides[2] and nutrient[3] analysis were planned to be collected monthly between November 2011 and April 2013. However, due to staff shortages, samples were not collected between December 2011 and April 2012. Dissolved iron (II) and dissolved organic carbon (DOC) analyses were added to the program in June 2012.

Bore water height was measured at all transect bores at 15 minute intervals between September 2011 and February 2013 (apart from a single bore at the Burdekin River). A Level Troll 300 data logger was used to collect the samples. A barometer was in place in one bore at the Haughton River in order to record barometric pressure and this was then used to compensate for changes in water level due to barometric fluctuations. Logger memory was full in February 2013. Rainfall data at Powerline (station number 033280) was obtained from the Bureau of Meteorology website (http://www.bom.gov.au/).

3.2. Sample Collection

Samples were collected using methods outlined in Australian Standard AS/NZA 5667.11:1998 – Water Quality Sampling – Guidance on Sampling of Groundwaters. Samples were collected using a Geotech portable bladder pump and physical and chemical parameters (pH, dissolved oxygen,

[2] List of analytes are presented in Appendix 1

[3] Ammonia as N, Phosphate as P, Oxidised Nitrogen as N

specific conductivity (SC) and temperature) were monitored with a HACH water quality sensor. New 3/8" low density polyethylene (LDPE) tube hosing and fresh bladders were used at each bore to ensure no cross contamination occurred. Water depth in each bore was measured using a water level meter and the amount of water in each bore was calculated using the formula:

$$\text{Bore volume (kL)} = h \times \pi r^2 \qquad (1)$$

where h is height of water column in the bore (m) above the depth of the bore and r is the radius of the bore (m).

Samples were collected after the bore volume had been purged three times and when physico-chemical parameters had stabilised.

Samples for nutrient and DOC testing were field filtered using a Sartorius 0.45 µm polysulfone filter, and all sampling equipment was washed three times using Milli-Q water supplied by the Chemistry Centre, Science Division, DSITIA. Pesticides samples were collected directly into 1 L amber glass jars. Samples for dissolved iron (II) were filtered immediately upon collection using a Sartorius 0.45 µm cellulose acetate filter and transferred to pre-prepared ferrazine tubes (supplied by the Chemistry Centre, Science Division, DSITIA). Nutrient, DOC and pesticide samples were stored in the dark on ice bricks in the field. Samples were freighted to the Ecosciences Centre, Dutton Park. On return to the office nutrient samples were frozen and pesticide samples were refrigerated. Samples for nutrient, DOC and ferrizine analysis were then transported to the Chemistry Centre and pesticide samples were transported to Queensland Health Forensic and Scientific Services (QHFSS) for analysis. A quality assurance and quality control program was undertaken which included trip and field blanks, sample spikes and sample duplicates.

3.3. Sample Analysis

Pesticide samples were analysed (at QHFSS) using solid phase extraction followed by Liquid Chromatography – Mass Spectroscopy (LCMS) (QHFSS method QIS 29937). A suite of pesticides was analysed using the method, which included the priority PSII pesticides. Limits of reporting were lowered from July 2012 after the method was modified. Limits of reporting for before and after the modification are summarised in Appendix 1.

Nutrient analyses were undertaken at the Chemistry Centre according to Standard Methods 4500-NO_3, I, 4500-NH_3 H, 4500-P G (APHA-AWWA-WPCF 2005), which are Flow Injection Analysis methods (colorimetric techniques). The DOC was analysed using method 5310 D APHA-AWWA-WPCF 2005. Iron (II) was analysed using a modified version of Stookey (1970). NO_3 data were reported as oxidised nitrogen (NO_x), which is a mixture of both nitrite (NO_2) and nitrate (NO_3). Nitrite is typically only at low concentrations and is short lived (Hunter 2012), and so it was presumed that all oxidised nitrogen was in the form of nitrate.

Science Delivery Chemistry Centre (Dutton Park, Queensland) and QHFSS (Coopers Plains, Queensland) laboratories are both accredited by the National Association of Testing Authorities (NATA, Australia) for the analyses conducted.

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Figure 1 Satellite image of groundwater monitoring sites.

4. Site Descriptions

4.1. Haughton River at Powerline

The transect through the Haughton River site located at Powerline runs from approximately 30 m from the river to 150 m from the river in the riparian zone (Table 1, Figure 2), with the established Department of Natural Resources and Mines (DNRM) bore (RN 11900212) being approximately 680 m from the river (Figure 2). According to the bore log, the bore closest to the river (RN 1900229) intercepts a silty clay layer (Figure 3), which would be expected to be fairly impermeable. The other two bores in the transect (RN 11900230 and RN 11900232) intercept silty sand and silt/gravel layers respectively (Figure 3). The minimum sampled depths range from 7.5 m to 8.5 m (from the top of the bore casing) (Table 1). In contrast, the established bore (11900212) had a minimum sampling depth of 18.8 m (Table 1), and is situated in a rocky, clay layer (Figure 3). This bore is surrounded by sugar cane fields and is in the vicinity of an irrigation channel (Figure 2).

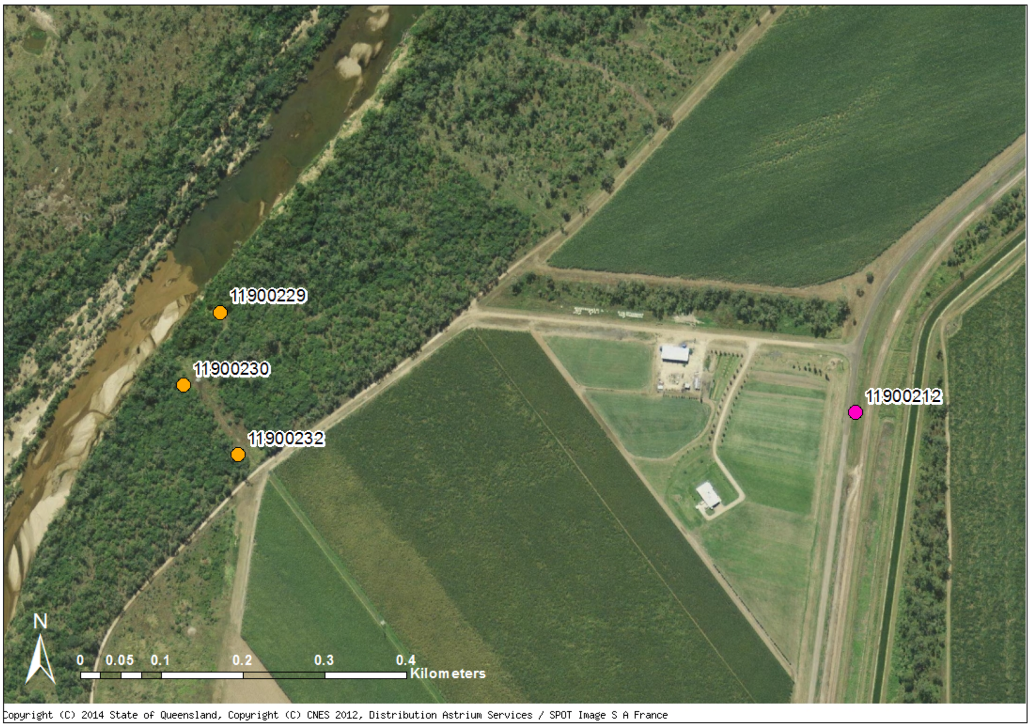


Figure 2 Position of monitoring bores at the Haughton River at Powerline. Yellow circles indicate National Water Commission (NWC) transect bores, the pink circle indicates an established Natural Resources and Mines (NRM) bore.

Table 1 Summary of depth of aquifer sampled and distance from river for each bore at Haughton River at Powerline.

Registered Bore Number	Sampled aquifer depth (m)	Approximate distance from Haughton River (m)
RN 11900229	8.5–10.5	30
RN 11900230	8.5–10.5	50
RN 11900232	7.5–9.5	150
RN 11900212	18.8–20.80	680

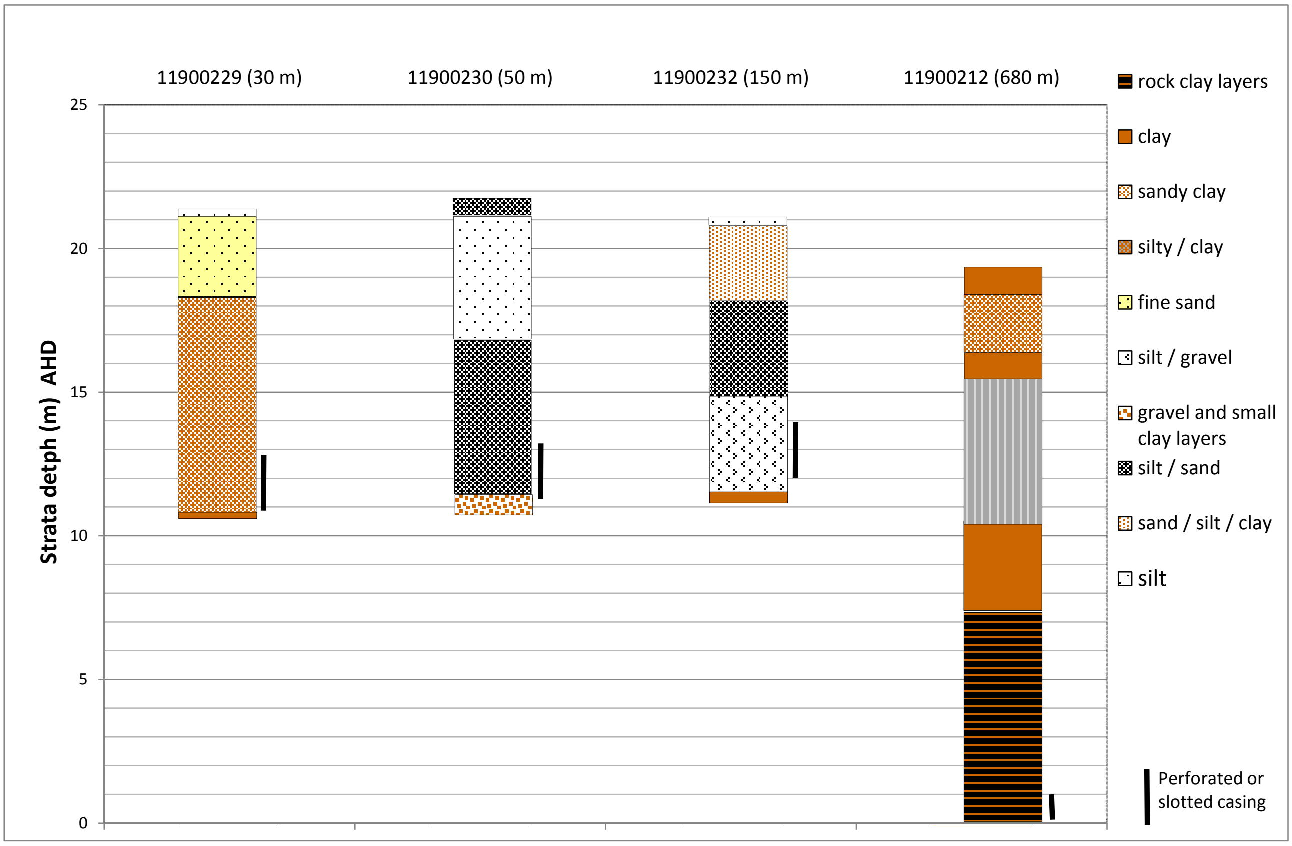


Figure 3 Bore strata details for the Haughton River site at Powerline.

4.2. Barratta Creek at Northcote

The transect at the Barratta Creek site located at Northcote extends from approximately 20 m from the river to 125 m from the river in the riparian zone (Table 2). The established DNRM bore (RN 11910204) was approximately 360 m from the river on the edge of sugar cane fields. According to the bore log, the bore closest to the river (RN 11911173) intercepts a gravel layer overlain with a less permeable silty/clay layer (Figure 5). RN 11911174 intercepts a silt clay layer, and RN 11911175 intercepts a fine sand layer (Figure 5). The minimum sampled depths range from 3.8 m to 5.5 m (from the top of the bore casing) (Table 2). In contrast, the established bore (RN 11910204) has a sampling depth of 12.5 m (Table 2), and is situated in a coarse sand and gravel layer (Figure 5).

Figure 4 Position of monitoring bores for Barratta Creek located at Northcote. Yellow circles indicate National Water Commission (NWC) transect bores, the pink circle indicates an established Natural Resources and Mines (NRM) bore.

Table 2 Summary of depth of aquifer sampled and distance from river for each Barratta Creek bore located at Northcote.

Bore Number	Sampled aquifer depth (m)	Distance from Barratta Creek (m)
RN 11911173	3.8–5.8	20
RN 11911174	4.0–6.0	50
RN 11911175	5.5–7.5	125
RN 11910204	12.5–13.0	360

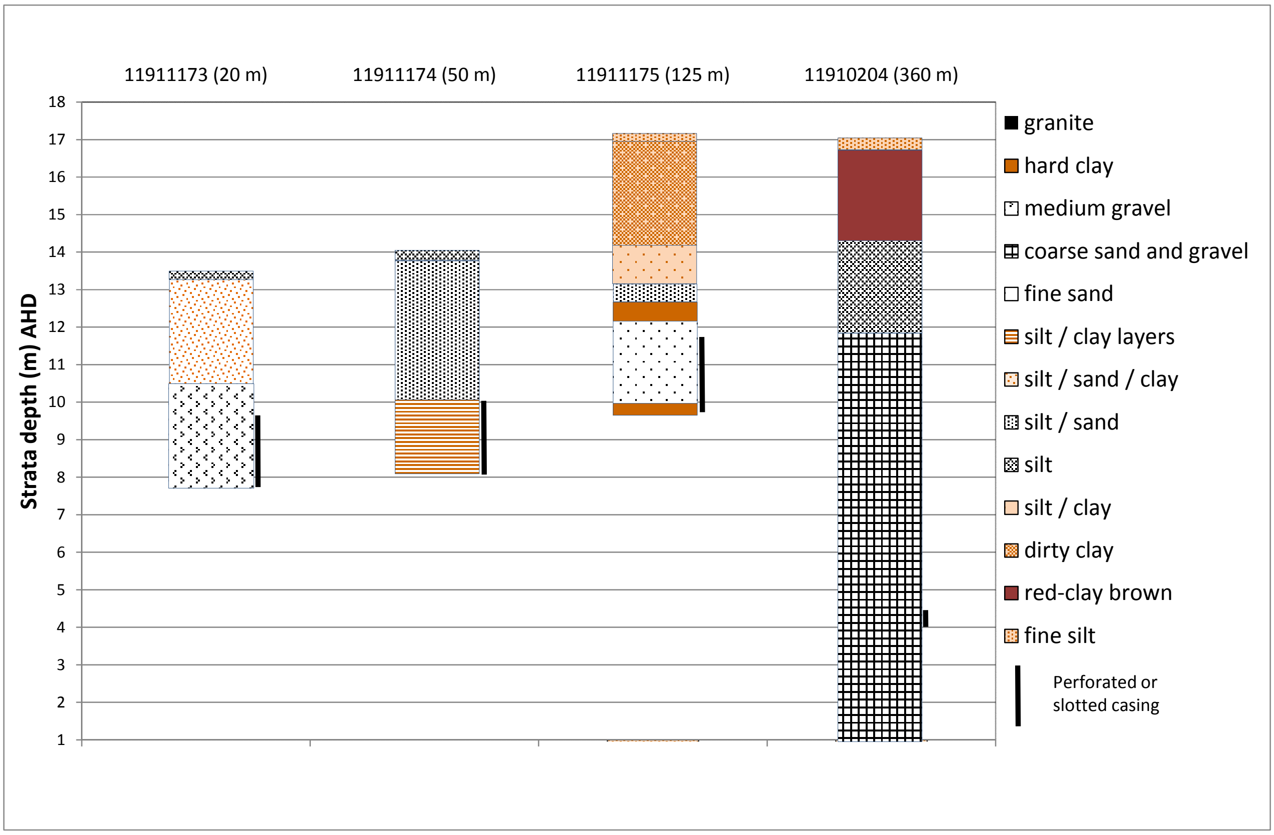


Figure 5 Bore strata details of the Barratta Creek site located at Northcote.

4.3. Burdekin River at Clare

The transect at the Burdekin River site located at Clare extends from approximately 50 m to 115 m from the river predominantly in a riparian zone (Table 3, Figure 6). The established DNRM bore (RN 12000168) is approximately 225 m from the river and situated in a field used for a variety of horticulture crops during the sampling period, although the general area is dominated by sugar cane. RN 12001396 and RN 12001397 drain silt sand layers, and bore RN 12001398 intercepts a silty layer (Figure 7). The minimum sampled depths range from 13.5 m to 14.7 m (Table 3). In contrast, the established bore (RN 12000168) has a sampling depth of 20.5 m (Table 3) and is situated in a silt/sand/clay layer (Figure 7).

Figure 6 Position of monitoring bores at the Burdekin River site located at Clare. Yellow circles indicate National Water Commission (NWC) transect bores, the pink circle indicates an established Natural Resources and Mines (NRM) bore.

Table 3 Summary of depth of aquifer sampled and distance from river for each bore located at the Burdekin River site at Clare.

Bore Number	Sampled aquifer depth (m)	Approximate distance from Burdekin River (m)
12001396	14.7–16.7	50
12001397	13.5–15.5	75
12001398	14.6–16.6	115
12000168	20.5–22.5	225

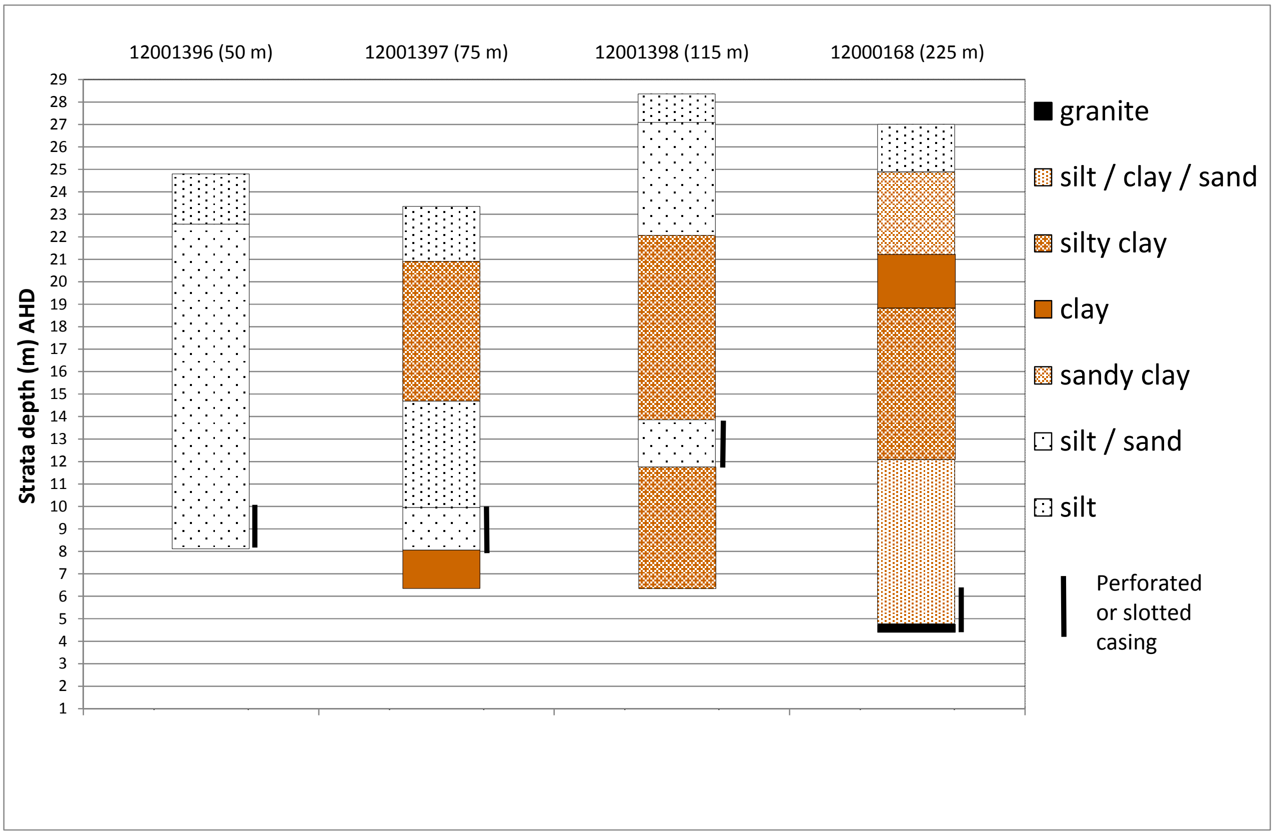


Figure 7 Bore strata details for the Burdekin River site at Clare.

4.4. Barratta Creek at Jerona

The single bore in the Barratta Creek at Jerona is located on the edge of the Ramsar listed Bowling Green Bay, in an area used for cattle grazing and sugar cane (Figure 8). The sampled depth was 9 m to 15 m and went through three stratigraphic layers (sand/clay, sand/silty clay, and clay sand (Figure 9). The bore is situated on the edge of an area known as the subterranean estuary (STE) which is the coastal portion of the Burdekin aquifer where fresh terrestrial groundwater meets an intruded seawater wedge (Lenahan 2012).

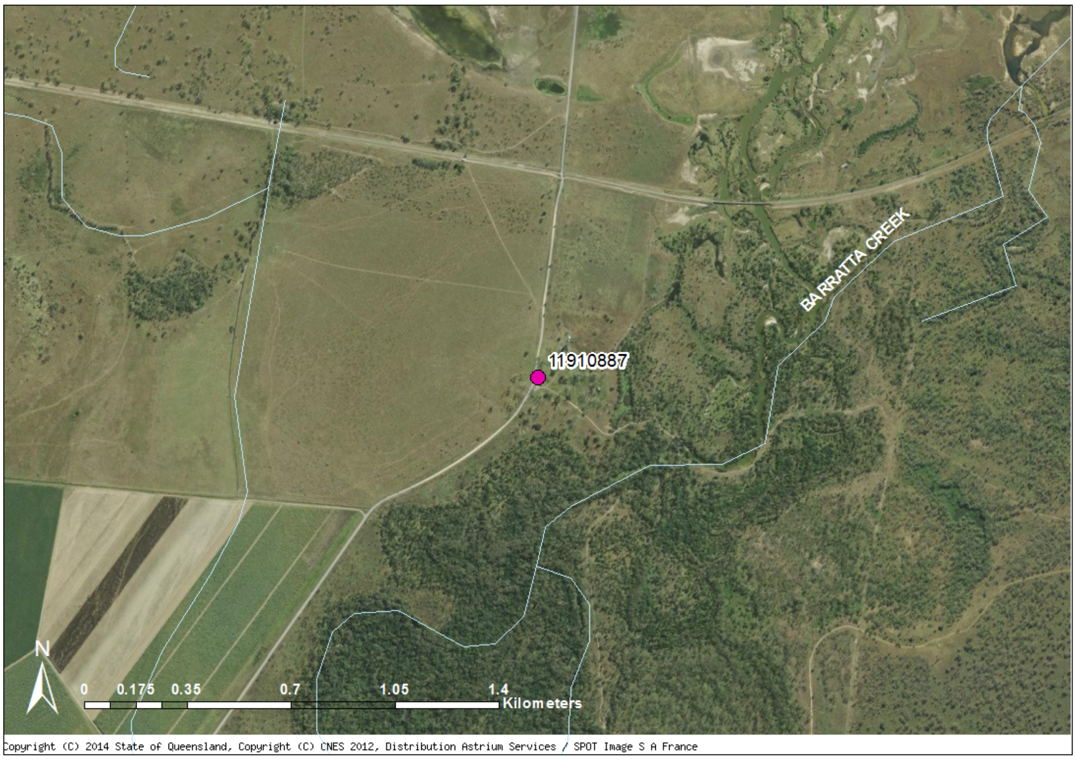


Figure 8 Position of the monitoring bore for Barratta Creek at Jerona Road. The pink circle indicates an established Natural Resources and Mines (NRM) bore

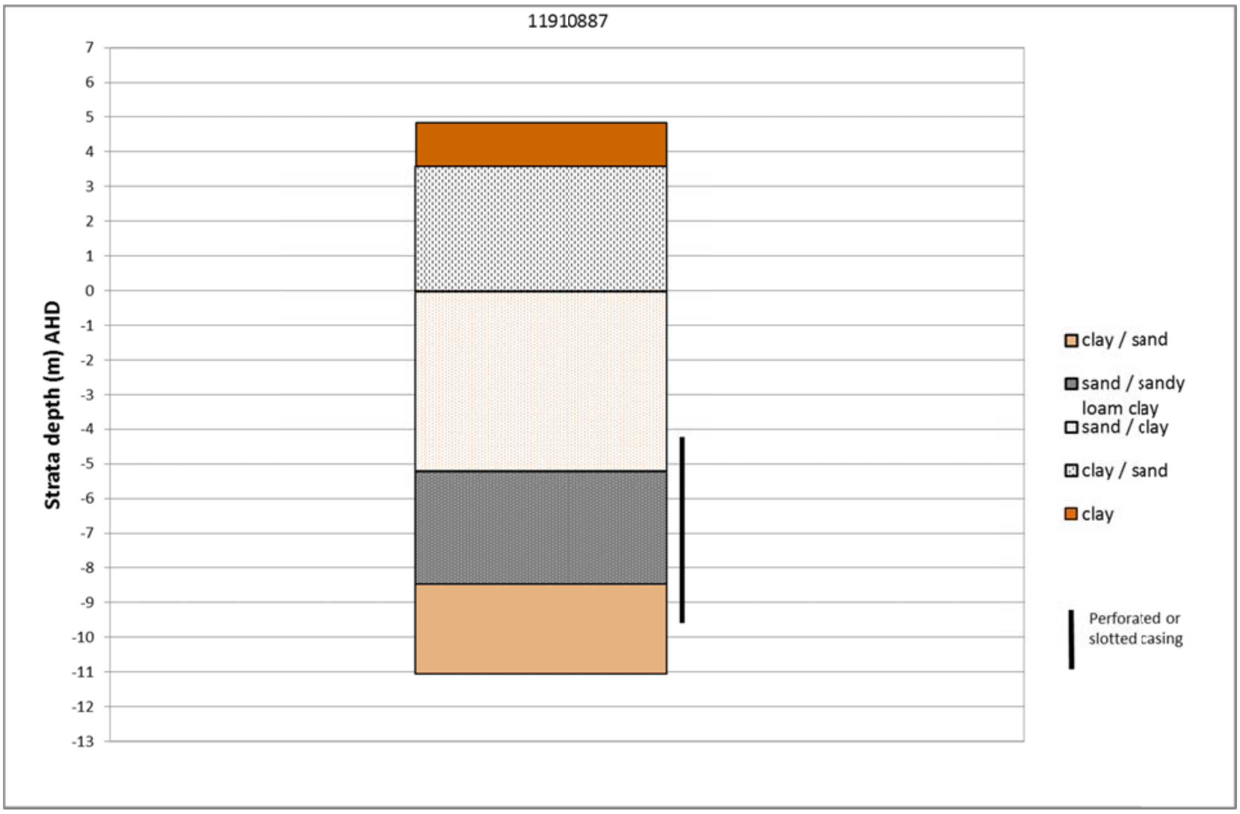


Figure 9 Bore strata details for the Barratta Creek at Jerona site.

5. Results and discussion

There were three distinct rainfall periods during the project that resulted in river flow rises - between December 2011 and March 2012, July 2012 and in January 2013 (Figure 10). Water levels in the bores in the riparian zone responded to varying degrees. There did not appear to be a relationship between water table and river height at the Haughton River site located at Powerline, although slight increases in the bore water heights did occur after heavy rainfalls in March 2012 and the end of January 2013 (Figure 10). At the Barratta Creek site at Northcote, there was a high degree of hydraulic connectivity with the bore closest to the creek (RN 11911173, 20 m from creek) with the water height in the bore mirroring the river height (Figure 11). This connectivity was not so apparent in the other two bores in the transect (RN 1191174 (50 m from creek) and RN 1191175 (125 m from creek)), although the water heights in the bores did increase following heavy rainfall and river flooding (Figure 11). The ground around bores RN 1191173 and RN 1191174 was flooded in March 2012, July 2012 and January 2013 (Figure 11). At the Burdekin River at Clare site, there appears to be some hydraulic connectivity with the bore closest to the river (RN 12001396, 50m from river) (Figure 12). The water height increased in this bore in a manner that reflected the slow rise in the river. RN 12001397 was less responsive to rainfall and river height.

The SC showed marked variation over time within individual bores and between bores. At the Haughton River site, there was distinct difference between the SC between bores with two groups of bores being apparent (Figure 13a). There was an increase in SC towards the river, with the two bores closest to the river having the highest SC (ranging between 821 and 1089 µS/cm) (Figure 13a), and the other two bores having SC values between 460 and 690 µS/cm) (Figure 13a). In contrast, the SC at the Burdekin River site at Clare generally decreased towards the river (Figure 13c), which is the converse of the results found by Lenahan (2012) at the same bores. At the Barratta Creek site at Northcote the SC was highly variable between bores indicating that each bore may be drawing from different aquifers (Figure 13b). The bore closest to the creek (RN 1191173) had a SC that varied between 1823 and 2402 µS/cm over the monitored period (Figure 13b), whereas the bore furthest away from the creek (RN 1191175) had a SC that varied between 314 and 4183 µS/cm (Figure 13b). It is interesting to note that the conductivity in this bore dropped from around 4000 µS/cm in January 2013 to 314 µS/cm in February 2013, indicating a large influx of low SC freshwater following rain in late January 2013. The SC measured in February 2013 at this bore (314 µS/cm) is consistent with the conductivity measured in Barratta Creek (100-250 µS/cm between 24 and 27 January 2013, the time of the Barratta Creek flood peak) (http://watermonitoring.derm.qld.gov.au/host.htm). This pattern also appeared to occur during the wet period between November 2011 and March 2012, as the May 2012 SC was markedly lower at 1668 µS/cm than the November 2011 value of 3134 µS/cm. The SC subsequently increased from this date onwards. As no data were collected between November 2011 and March 2012 it is not possible to be definitive. However, consistent with the idea that high rainfall or river flood waters decreased the SC, the SC gradually increased after the wet period (Figure 13b). The lowest salinity at Barratta Creek at Northcote was measured in the middle bore of the transect (RN 1191174) which ranged between 454 and 746 µS/cm (Figure 13c). The SC at Barratta Creek at Jerona showed gradual changes over time, ranging between 3901 and 4779 µS/cm (Figure 13d). pH was circumneutral at all sites (Appendices 2 to 5).

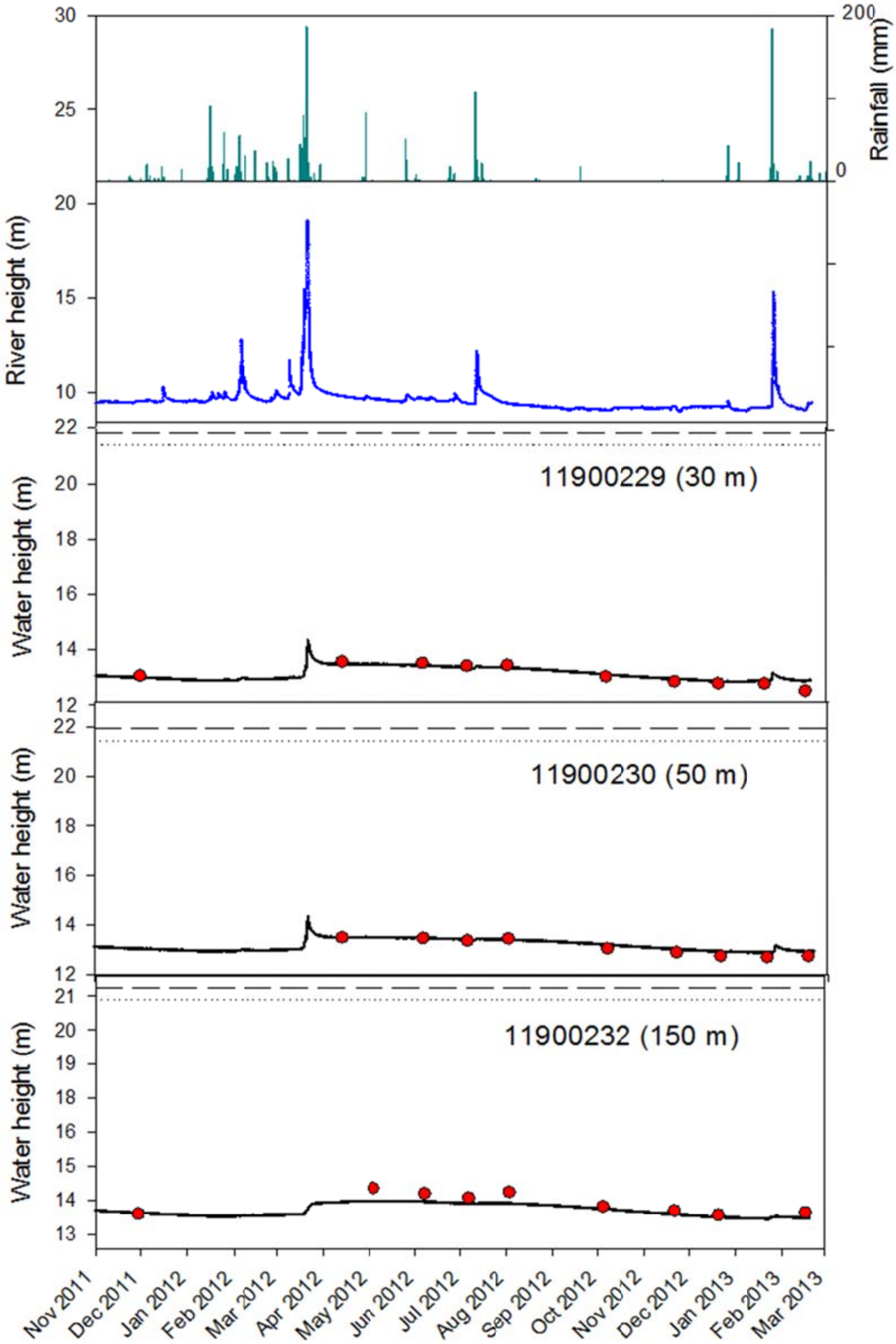


Figure 10 Rainfall (histogram), river height and groundwater depth at the Haughton River at Powerline site between November 2011 and April 2013. Red dots are water heights measured at time bores were sampled. Long dashes indicate the height of the bore, dotted lines indicate the ground height at the bore. All height data are expressed in terms of Australian Height Datum (AHD).

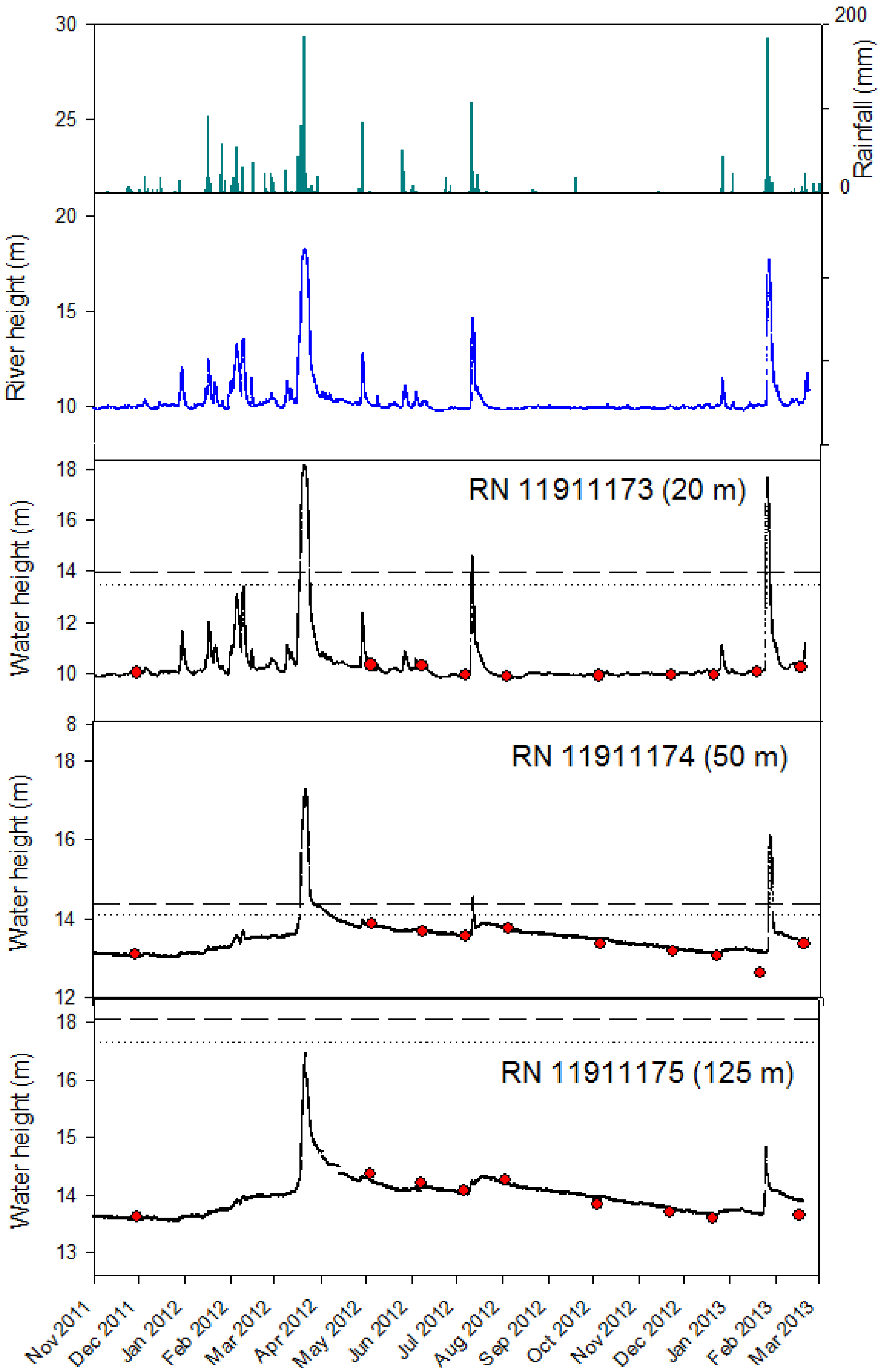


Figure 11 Rainfall (histogram), river height and groundwater depth at the Barratta Creek at Northcote site between November 2011 and April 2013. Red dots are water heights measured at time bores were sampled. Long dashes indicate the height of the bore, dotted lines indicate the ground height at the bore. All height data are expressed in terms of Australian Height Datum (AHD).

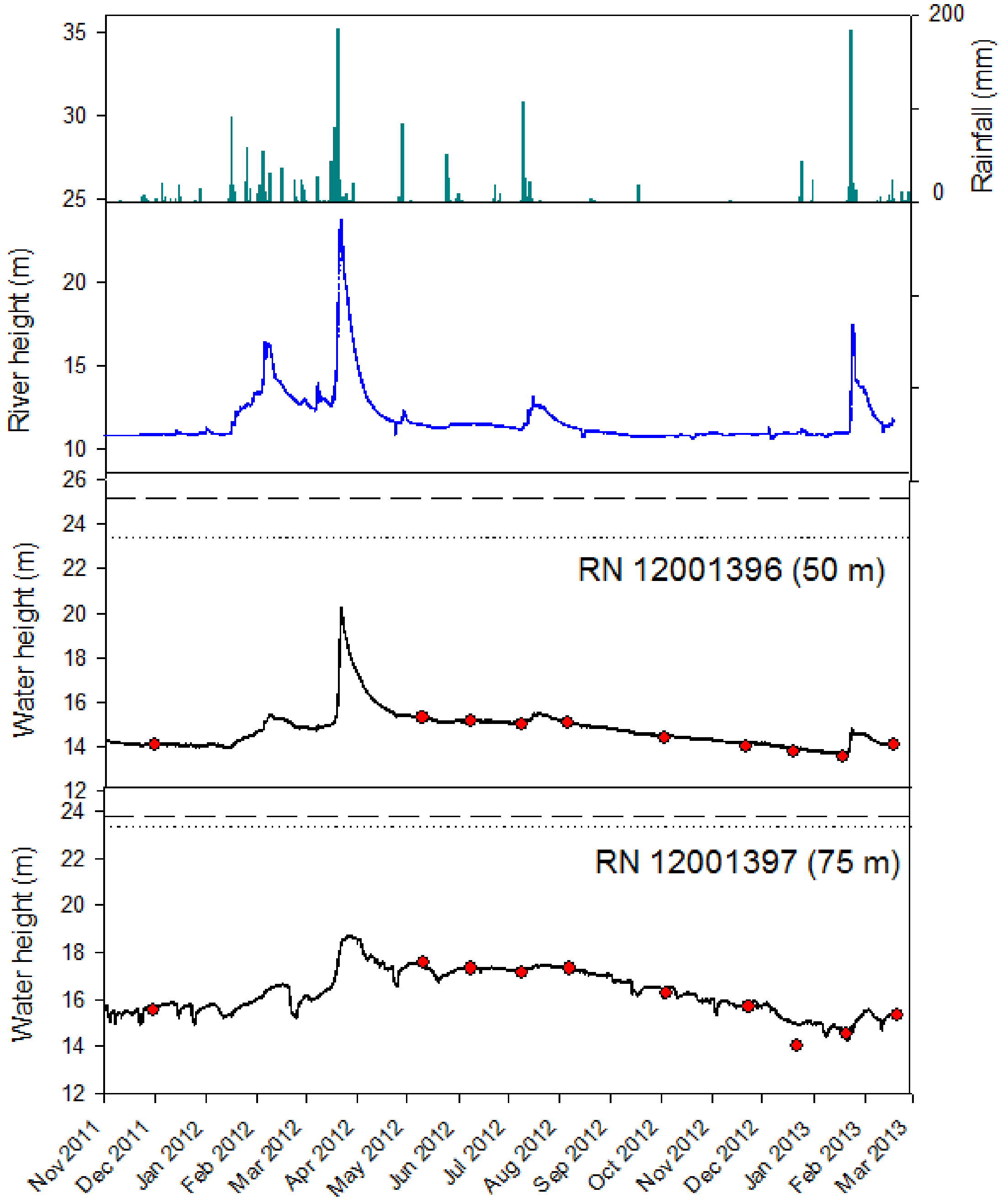


Figure 12 Rainfall (histogram), river height and groundwater depth at the Burdekin River at Clare site between November 2011 and April 2013. Red dots are water heights measured at time bores were sampled. Long dashes indicate the height of the bore, dotted lines indicate the ground height at the bore. All height data are expressed in terms of Australian Height Datum (AHD).

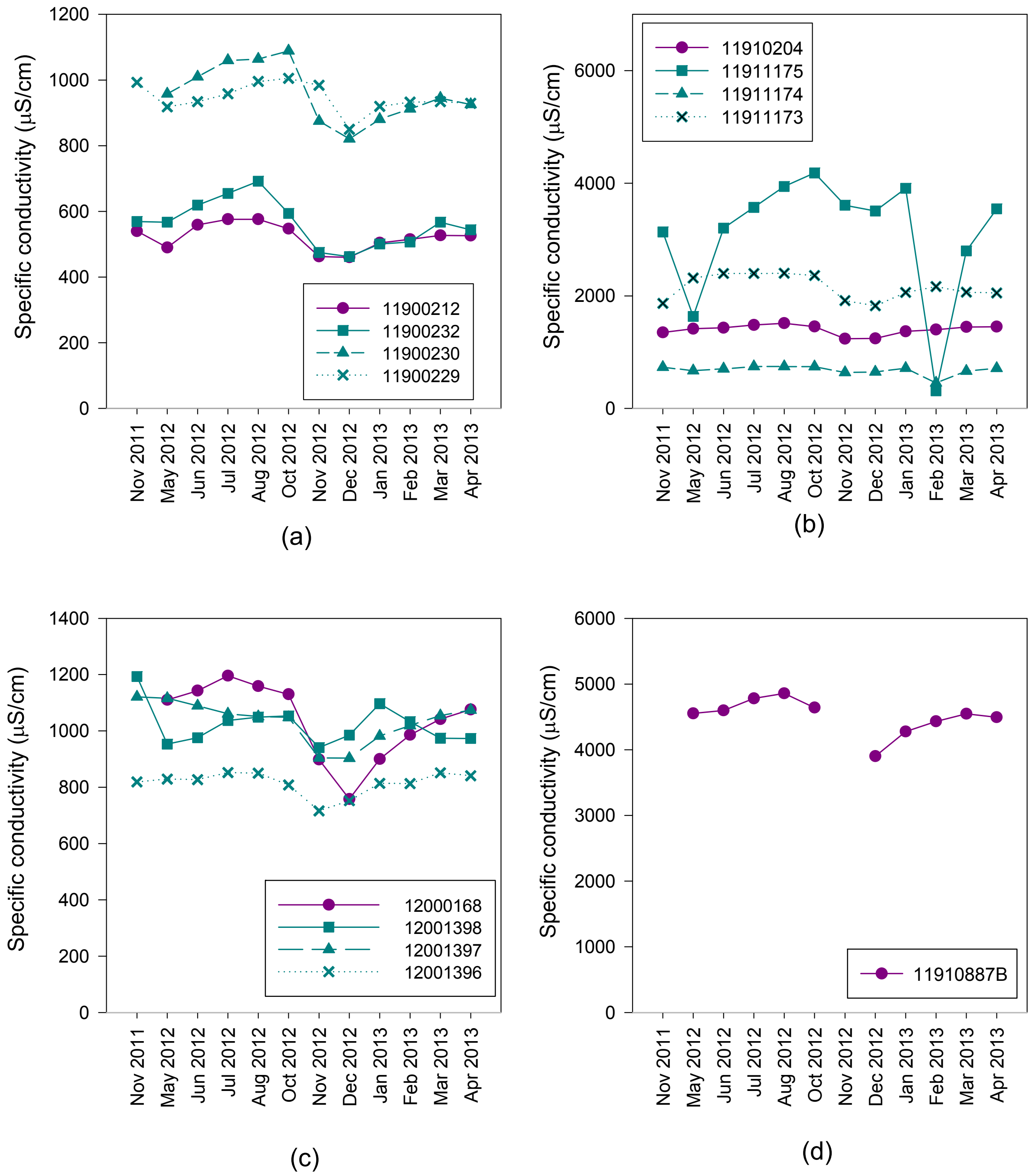


Figure 13 Specific conductivity measured in bores at (a) Haughton River at Powerline (b) Barratta Creek at Northcote (c) Burdekin River at Clare and (d) Barratta Creek at Jerona, between November 2011 and April 2013.

5.1. Nutrients

5.1.1. Comparison to Guidelines

Median concentrations[4] of oxidised nitrogen, ammonium and phosphate were compared to the Queensland Water Quality Guidelines (QWQGs) (DEHP 2009) (Table 4 to Table 7) for the Central Coast Region and the 95th percentile[5] of oxidised nitrogen and ammonium concentrations were compared to the Australian and New Zealand water quality guideline TVs for the protection of aquatic ecosystems (Table 4 to Table 7), as both these compounds are considered to be toxicants (ANZECC and ARMCANZ 2000). Neither set of guidelines are flow referenced. Two aspects should be noted in regards to the toxicity values. Firstly, the TV for ammonia is pH and temperature dependent, and the guideline value quoted is for waters with a pH of 8 (temperature is not taken into account) (ANZECC and ARMCANZ 2000). As the toxicity of ammonia decreases with decreasing pH, and the pH of the measured groundwater at all sites was 7.5 or less (Appendices 2 to 5), the TV in the guidelines (ANZECC and ARMCANZ 2000) was used as a point of first comparison. Secondly, oxidised nitrogen contains both nitrate and nitrite fractions. However, nitrite if present is typically present at low concentrations and is short-lived (Hunter 2012) and so an assumption was made that all oxidised nitrogen was present as nitrate.

The median concentration of nitrate was above the QWQGs (DEHP 2009) and TVs at all the Haughton River bores (Table 4). In contrast, the concentration of ammonium did not exceed the guidelines in any of the bores and was only measured at relatively low concentrations at the Haughton River site (Table 4). The median concentration of phosphate also exceeded the QWQGs (DEHP 2009) at three of the four bores at the Haughton River (Table 4). Overall, the concentration of nitrate and phosphate at this site were in the same order of magnitude as previously reported (Lenahan 2012).

The nitrogen species in the bores of the transect at the Barratta Creek site located at Northcote (RN 11911175, RN 1191174 and RN 1191173) were predominantly in the form of ammonium, at concentrations above the QWQGs (DEHP 2009) (Table 5). The concentration of ammonium exceeded the TV (for pH 8) at RN 1191173, the bore closest to Barratta Creek. However the pH at this bore ranged between 6.5 and 7, equating to an ammonium-N TV ranging between 2.18 and 2.46 mg/L. The 95th percentile at this site was 1.3 mg/L and so the pH adjusted ammonium TV was not exceeded.

Both ammonium-N and nitrate-N were present in all bores at the Burdekin River site located at Clare, with the concentrations of ammonium being highest in the bore closest to the river bank (RN 12001396). Nitrate-N concentrations were the highest at this site, with the median concentration of nitrate-N at the established deep bore (12000168) being 6.6 mg/L, exceeding QWQGs by approximately 100 times, and ANZECC and ARMCANZ TVs by 30 times. Concentrations of nitrate-N have been recorded in the lower Burdekin at this level or higher previously, with a cluster of high nitrogen concentrations found in the Burdekin River between Clare and Mt Kelly (Barnes et al. 2005).

The median concentrations of both ammonium as N and phosphate as P exceeded the QWQGs (DEHP 2009) at the Barratta Creek at Jerona site, and ammonium as N was just below the ANZECCC and ARMCANZ TV (Table 7). Very low concentrations of nitrate as N were measured at this site, ranging from 0.001 mg/L to 0.006 mg/L.

[4] QWQGs Appendix D (D.2.2) states to used median concentrations for physico-chemical indicators
[5] ANZECC and ARMCANZ (section 7.4.4.2) states that 95th percentile of a data set should be used for toxicants

Table 4 Comparison of nutrient data collected from bores at Haughton River at Powerline between November 2011 and April 2013, the Australian and New Zealand Trigger Values for toxicants and the Queensland Water Quality Guidelines. Number of samples at each bore = 12. Cells with data from the bores that are shaded pink and orange contain values that are greater than the Queensland and Australian and New Zealand water quality guidelines, respectively.

Borehole		Ammonium nitrogen as N (mg/L)	Oxidised nitrogen as N (mg/L)	Phosphate phosphorus as P (mg/L)
QWQG		0.02	0.06	0.02
ANZECC and ARMCANZ (2000)		0.9	0.2*	
RN 11900212	Range	<0.004-0.008	0.798-2.81	0.054-0.142
	Median	0.002	1.170	0.113
	95th percentile	0.007	2.310	
RN 11900232	Range	<0.004-0.005	1.56-2.76	0.052-0.083
	Median	0.002	2.615	0.072
	95th percentile	0.004	2.749	
RN 11900230	Range	<0.004-0.012	0.013-0.755	0.002-0.011
	Median	0.005	0.146	0.005
	95th percentile	0.011	0.688	
RN 11900229	Range	<0.004-0.009	1.14-1.91	0.059-0.168
	Median	0.002	1.590	0.118
	95th percentile	0.0088	1.845	

*Guideline TV for nitrate (700 µg/L) (ANZECC and ARMCANZ 2000) converted using a conversion factor of 4.427

Table 5 Comparison of nutrient data collected from bores at Barratta Creek at Northcote between November 2011 and April 2013, the Australian and New Zealand Trigger Values for toxicants and the Queensland Water Quality Guidelines. Number of samples at each bore = 12. Cells with data from the bores that are shaded pink and orange contain values that are greater than the Queensland and Australian and New Zealand water quality guidelines, respectively.

Borehole		Ammonium nitrogen as N (mg/L)	Oxidised nitrogen as N (mg/L)	Phosphate phosphorus as P (mg/L)
QWQG		0.02	0.06	0.02
ANZECC and ARMCANZ (2000)		0.9	0.2**	
RN 11910204	Range	<0.004-0.011	0.949-1.27	0.007-0.033
	Median	0.0025	1.135	0.017
	95th percentile	0.007	1.259	
RN 11911175	Range	0.01-0.159	<0.001-0.083	0.012-0.127
	Median	0.066	0.004	0.037
	95th percentile	0.157	0.041	
RN 11911174	Range	0.03-0.13	0.002-0.009	0.088-0.136
	Median	0.043	0.003	0.115
	95th percentile	0.114	0.006	
RN 11911173	Range	0.852-1.3	0.004-0.03	<0.001-0.001
	Median	1.020	0.009	0.0005
	95th percentile	1.3	0.0245	

*Guideline TV for nitrate (700ug/L) (ANZECC and ARMCANZ 2000) conversion factor of 4.427

Table 6 Comparison of nutrient data collected from bores at the Burdekin River at Clare between November 2011 and April 2013, the Australian and New Zealand Trigger Values for toxicants and the Queensland Water Quality Guidelines. Number of samples at each bore = 12, apart from 12000168 where only 11 samples were collected. Cells with data from the bores that are shaded pink and orange contain values that are greater than the Queensland and Australian and New Zealand water quality guidelines, respectively.

Borehole		Ammonium nitrogen as N (mg/L)	Oxidised nitrogen as N (mg/L)	Phosphate phosphorus as P (mg/L)
QWQG		0.02	0.06	0.02
ANZECC and ARMCANZ (2000)		0.9	0.2**	
12000168	Range	<0.004-0.004	2.62-7.79	0.004-0.017
	Median	0.002	6.620	0.006
	95th percentile	0.003	7.695	
12001398	Range	<0.004-0.024	0.041-0.123	0.009-0.037
	Median	0.004	0.106	0.026
	95th percentile	0.017	0.122	
12001397	Range	<0.004-0.005	2.38-4.54	0.047-0.178
	Median	0.002	3.920	0.139
	95th percentile	0.005	4.447	
12001396	Range	0.103-0.145	0.324-0.817	<0.001-0.036
	Median	0.125	0.491	0.002
	95th percentile	0.1417	0.7752	

*Guideline trigger value for nitrate (700ug/L) (ANZECC and ARMCANZ 2000) conversion factor of 4.427

Table 7 Comparison of nutrient data collected from the bore at Barratta Creek at Jerona Road between November 2011 and April 2013, the Australian and New Zealand Trigger Values for toxicants and the Queensland Water Quality Guidelines. Number of samples at each bore = 12, apart from 12000168 where only 11 samples were collected. Cells with data from the bores that are shaded pink and orange contain values that are greater than the Queensland and Australian and New Zealand water quality guidelines, respectively.

Borehole		Ammonium nitrogen as N (mg/L)	Oxidised nitrogen as N (mg/L)	Phosphate phosphorus as P (mg/L)
QWQG		0.02	0.06	0.02
ANZECC and ARMCANZ (2000)		0.9	0.2*	
RN 11910887	Range	0.039-0.131	0.001-0.006	0.025-0.086
	Median	0.103	0.002	0.076
	95th percentile	0.12	0.005	

*Guideline trigger value for nitrate (700ug/L) (ANZECC and ARMCANZ 2000) conversion factor of 4.427

5.1.2. Nutrient concentrations change through the riparian zone

It is thought that leaching and deep drainage of nitrogen predominantly occurs as nitrate, with denitrification being the main mechanism for removing nitrate from subsurface soils (Hunter 2012). Denitrification through the riparian zone in the agricultural landscape has been described in a number of studies (e.g. Haycock and Pinay 1993; Bruschh and Nilsson 1993, Cooper 1990 cited in Hill 1996), however most of these studies have been undertaken in humid temperate zones (Lamontagne et al. 2005). Denitrification is the process whereby nitrate is converted to nitrogen gas (N_2) under anaerobic conditions, with dissolved oxygen concentrations of <1-2 mg/L, an oxidation redox potential (ORP) of +230 mV or lower and the presence of bioavailable carbon (Hunter 2012 and references therein). Thomassson et al. (1991) (cited in Keating et al. 1996) state that an organic carbon content above 2 mg/L is necessary for denitrification to occur. In addition, the depletion of nitrate from groundwater appeared to occur in shallow aquifers, with Haycock and Burt (1993) cited in Hill (1996) finding that depletion of nitrate occurred mostly in the top 5 to 8 m of groundwater flow, with other studies mostly being in shallow aquifers (less than a few meters) (Hill 1996). The potential for riparian zones to remove nitrate from groundwater is based on the supposition that organic carbon concentrations are much higher and extend deeper in riparian areas with deep rooted and dense vegetation than the vegetation in adjacent fields (Hunter 2012). Mean DOC concentrations measured during this study tended to be lower than 2 mg/L (Figure 14), apart from at Barratta Creek site located at Northcote where elevated levels of DOC were measured at RN 11911175 and RN 11911174 after the January 2013 rainfall event (Figure 15). The DOC measured at RN 1191173 was relatively low (Figure 15) ranging between 0.9 and 3.5 mg/L throughout the monitoring period, with concentrations of DOC only being higher than 2 mg/L in three months (October to December 2012). This does not indicate that elevated DOC is present for prolonged periods in the riparian zone. The available data does not provide any consistent evidence that there is sufficient DOC to support consistent denitrification, although DOC levels could increase as a result of high rainfall and flooding.

Alternatively, if bioavailable carbon is not present, reduced forms of manganese, iron (e.g. Fe (II)) and sulphur can be used by some microbes in the denitrification process (Korom 1992 cited in Hunter 2012). Fe (II) was only elevated at the two bores closest to the creek in the Barratta Creek site at Northcote (RN 11911174 and RN 119111793) (Figure 14), and the bore closest to the creek at the Burdekin River site at Clare (RN 12001396) (Figure 14). Concentrations of Fe (II), where detected, were highly variable (Figure 16 and Figure 17). Mean ORP readings at all sites were in the range (≤+230 mV) at which denitrification can occur (Figure 18), with reducing conditions (negative ORP values) prevalent at the bores closest to the river bank at the Barratta Creek site at Northcote and the Burdekin River site at Clare.

Lenahan (2012) developed a reactive transport model in the Burdekin to assess the role of the aquifers in transporting nitrogen to the reef via aquifer discharge zones, including areas where groundwater was known to discharge through the riparian areas. He found that redox boundaries were present near Barratta Creek and Burdekin River, where dissolved oxygen decreased and electron donors (Fe II, Mn II and DOC) increased towards the creek, conditions which are favourable conditions for denitrification. These results were confirmed in this study. Based on modelling, Lenahan (2012) calculated that nitrate would undergo denitrification in the riparian zone prior to discharge, although he does caution that these conclusions were drawn from the single round of sampling. Based on the data collected in the current report, there is evidence of denitrification occurring in the riparian zones of the Barratta Creek and Burdekin River sites, as the mean nitrate concentrations at these sites decreased significantly towards the river bank (Figure 19). However, contrary to this, it is thought that the groundwater flow rate in the area may be too high for denitrification to occur, particularly in the Barratta Creek area (Roger Shaw pers. comm.).

At the same time, ammonium increased in concentration towards the river bank, particularly at the Barratta Creek site (Figure 19). Ammonium is not a product of denitrification, but can be produced as the result of a process known as dissimilatory nitrate reduction to ammonium (DNRA). This may be the mechanism for the increase in ammonium towards the river bank at the Barratta Creek and

Burdekin River sites. However, Lenahan (2012) stated that the ammonium detected in riparian groundwater was unlikely to be the result of DNRA as this process is more common in systems where DOC is the principal electron donor. Supporting his argument Lenahan (2012) found that Fe^{2+} and Mn^{2+} were the principal electron donors in Barratta Creek and the Burdekin River. Rutting et al. (2011) found that a high carbon to nitrogen ratio is needed for DNRA to occur. The DOC measured in the groundwater where nitrate was present was relatively low, indicating that transformation of nitrate-N to ammonium-N is unlikely via DNRA. Lenahan (2012) hypothesised that the elevated ammonium concentrations in the Burdekin River and Barratta Creek riparian zones were due to decomposition of organic material (Lamontagne et al. 2005; Lamontagne et al. 2006). However, this does not explain the lack of ammonium in the Haughton River riparian zone where, presumably, decomposition of organic material would also occur.

In general, the results presented by Lenahan (2012) were confirmed in this study. Lenahan (2012) also noted that results from the Haughton River riparian zone were inconclusive as the patterns of decreased dissolved oxygen and increased electron donors were not evident in this area, and suggested that disturbance to the aquifer from bore drilling may have influenced the results. It is unlikely that over the extensive period that that this site was monitored during the present study that this is the case, and that different processes were occurring through the riparian zone in the Haughton River site at Powerline.

It is generally considered that phosphate is not transferred via groundwater to surface waters, as phosphate tends to sorb to soils or precipitate out and does not leach (Hunter 2012). However, if soils are acidic, sandy or supersaturated with phosphate, leaching can occur (Hunter 2012). This study found that similarly to nitrate, phosphate was not present in the groundwater of bores closest to Barratta Creek or Burdekin River (Figure 19), indicating geochemical processes may be precipitating phosphate onto the soil in the riparian zone. Lenahan (2012) suggests this may occur when Fe (II) is oxidised to Fe (III), as iron (III) and phosphate will coprecipitate.

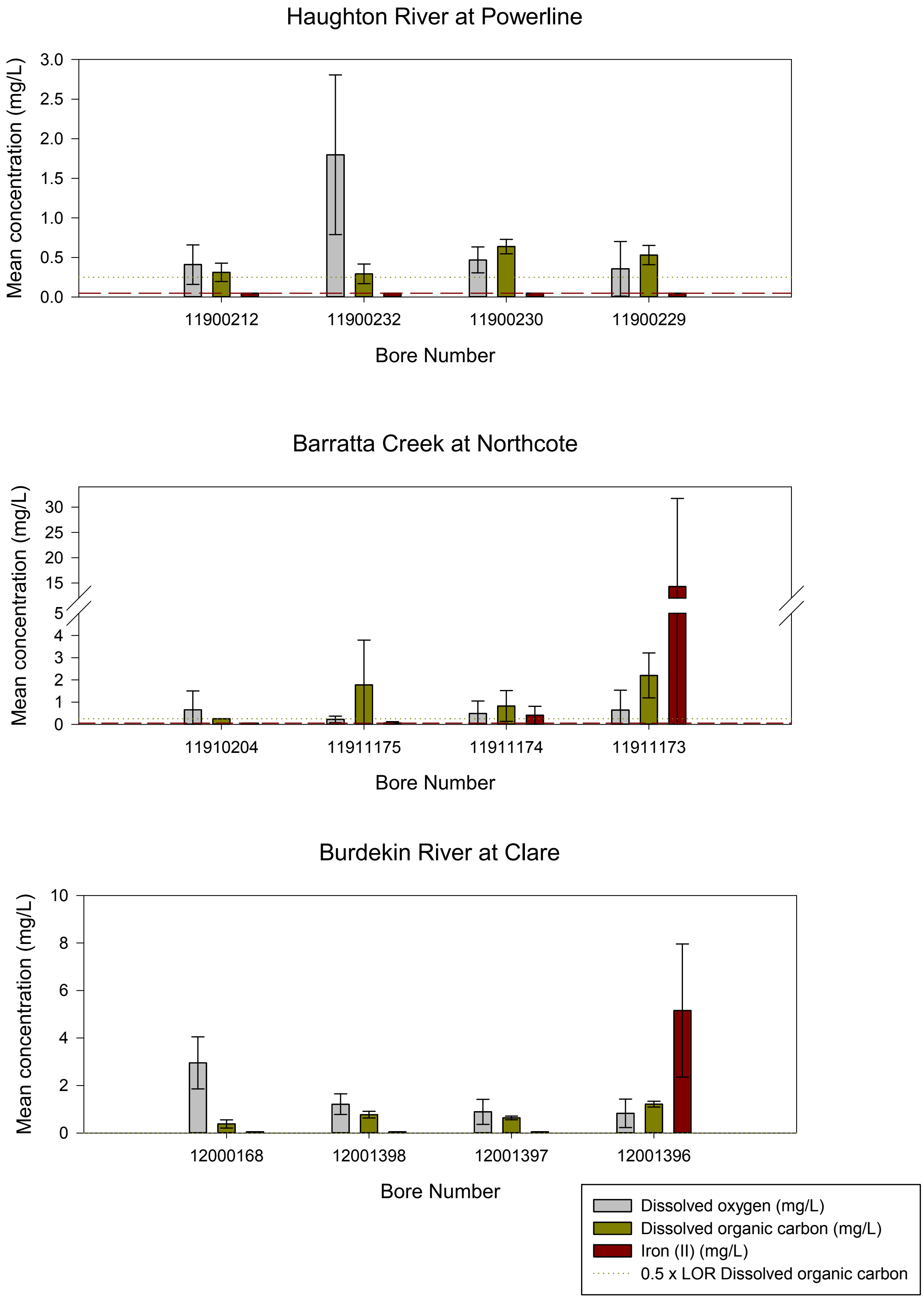


Figure 14 Mean (± standard deviation) dissolved oxygen, dissolved organic carbon and iron (II) concentrations measured in bores at the Haughton River site at Powerline, the Barratta Creek site at Northcote and the Burdekin River site at Clare between November 2011 and April 2013 Note: Bores to the left of the graphs are furthest away from river, bores to the right of graphs are closest. Twelve samples were collected at each site, apart from RN 12000168 where eleven samples were collected.

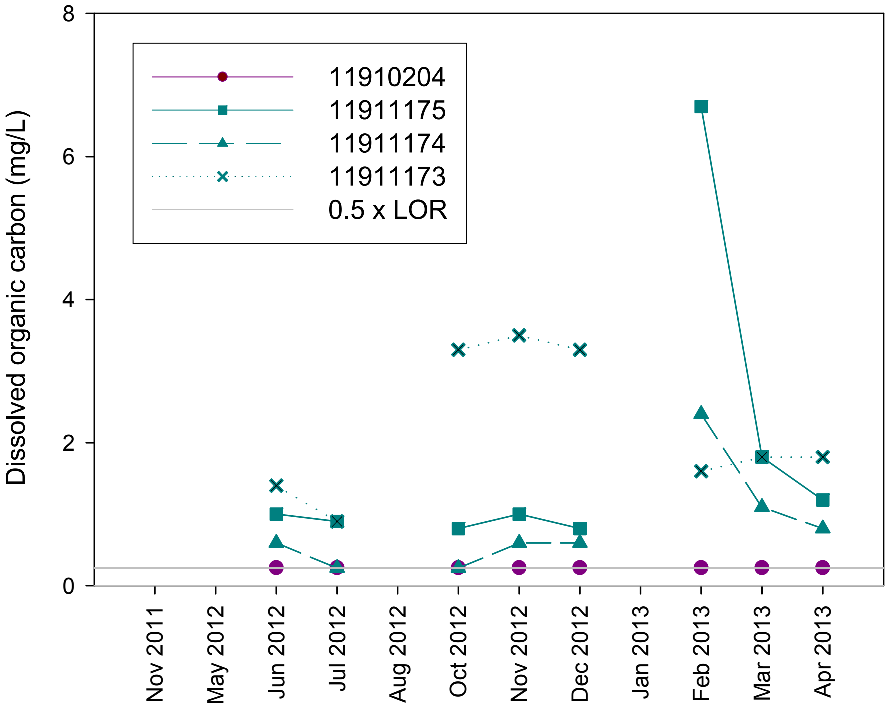


Figure 15 Dissolved organic carbon at the Barratta Creek site at Northcote between June 2012 and April 2013.

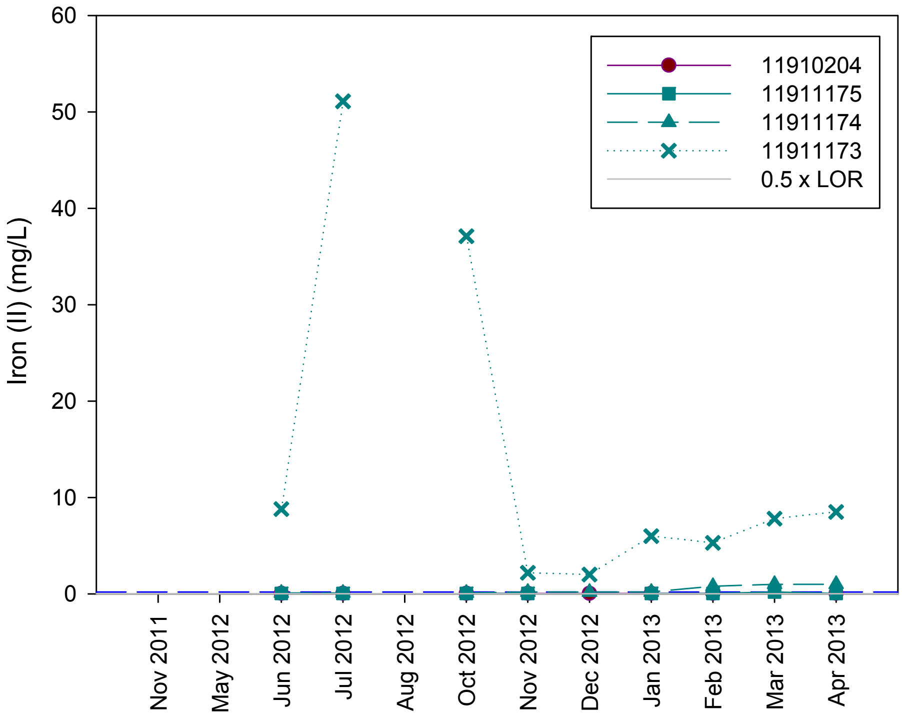


Figure 16 Iron (II) concentrations at the Barratta Creek site located at Northcote between June 2012 and April 2013.

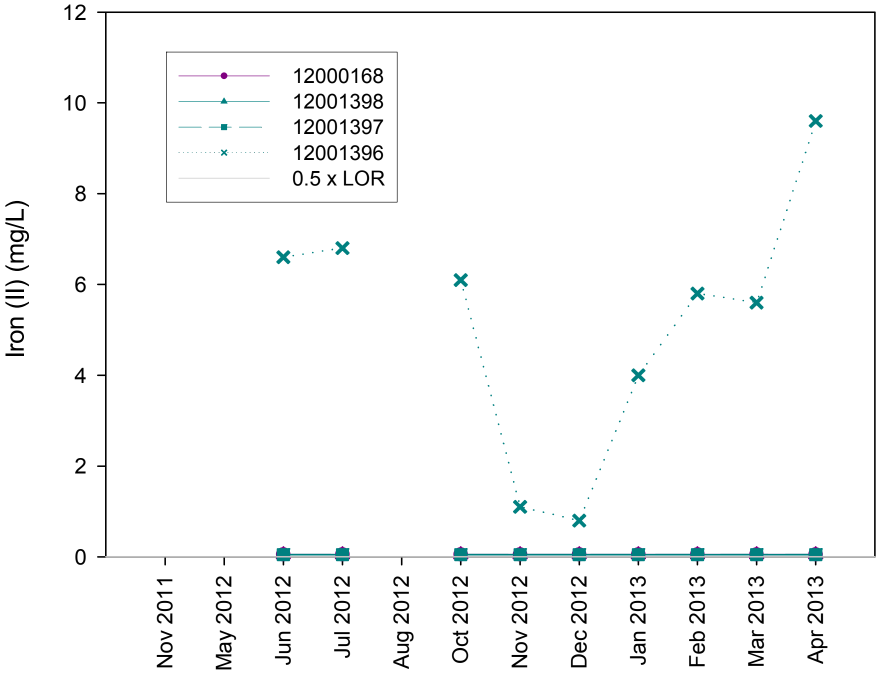
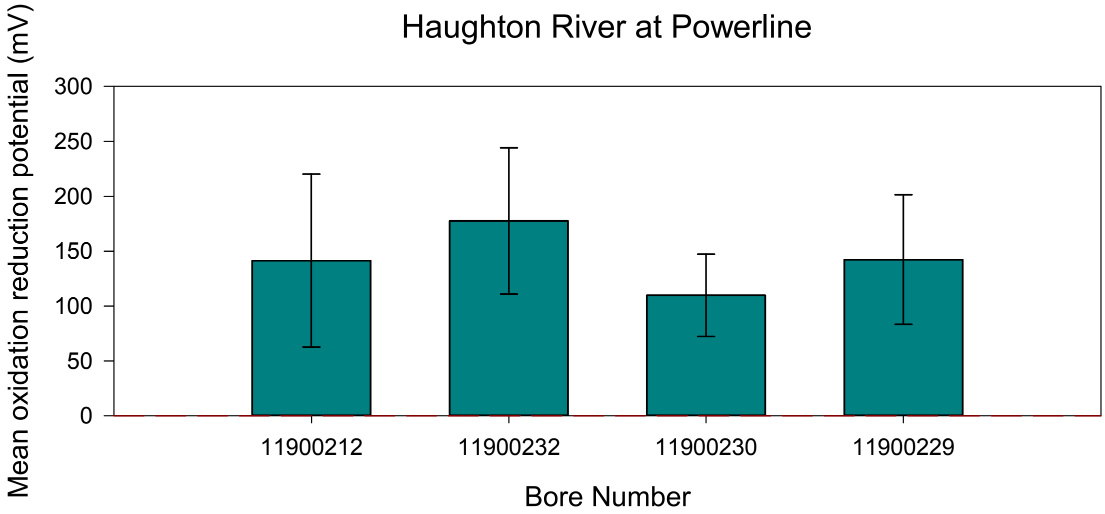
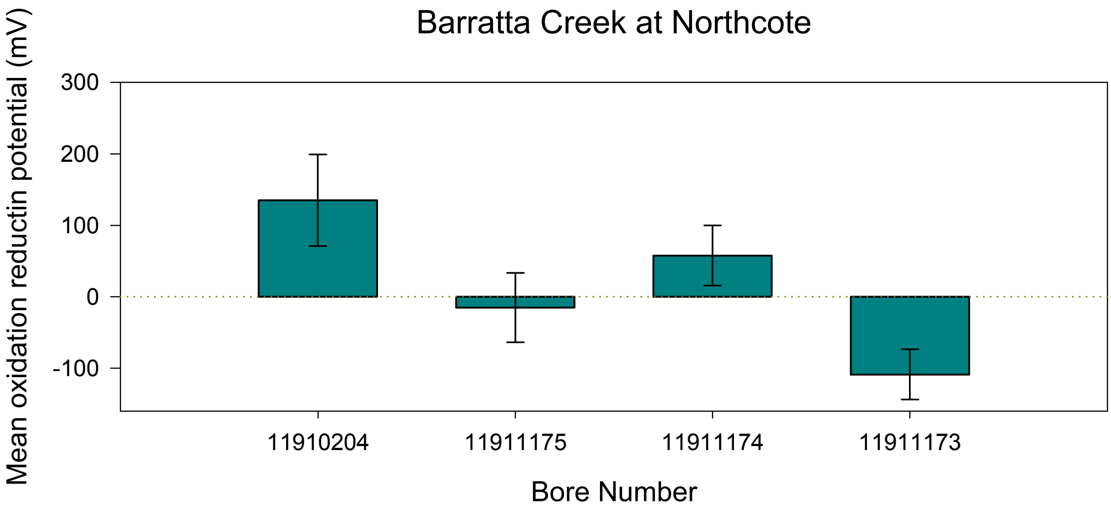


Figure 17 Iron (II) concentrations at the Burdekin River site located at Clare between June 2012 and April 2013.





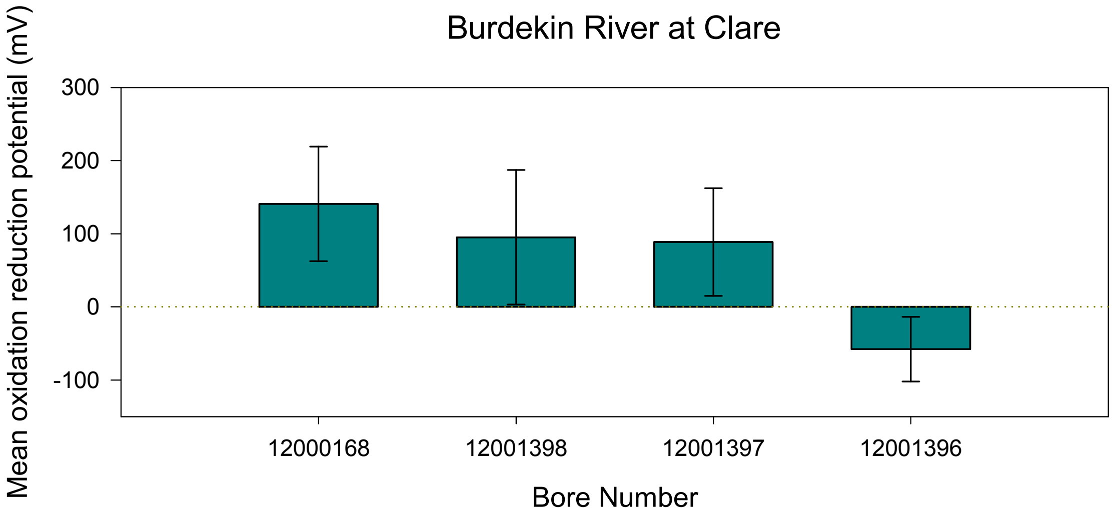


Figure 18 Mean (± standard deviation) oxidation reduction potential values in bores at the Haughton River site located at Powerline, the Barratta Creek site at Northcote and the Burdekin River site at Clare between November 2011 and April 2013. Twelve measurements were taken at each site, apart from RN 12000168 where eleven measurements were taken.

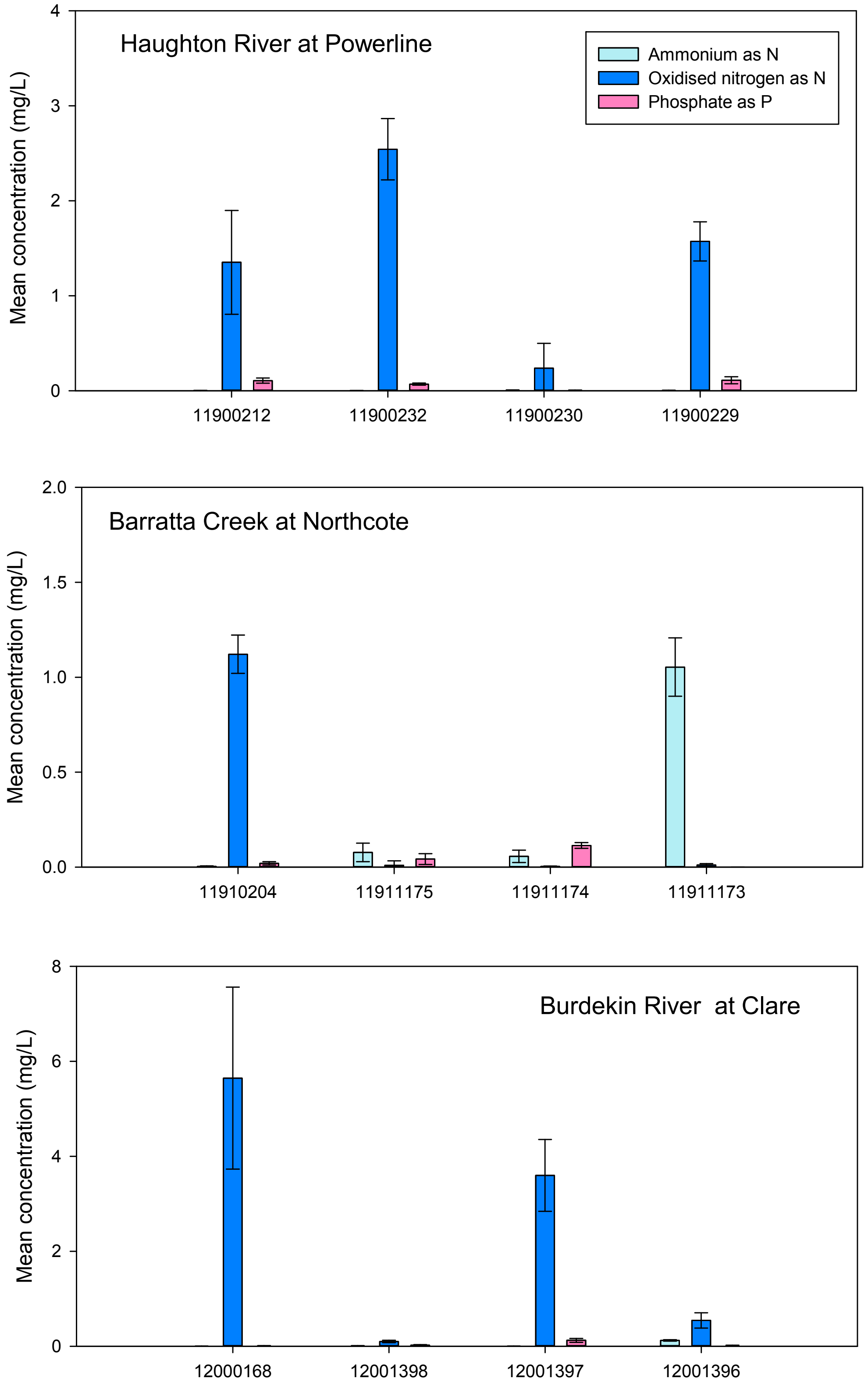


Figure 19 Mean (± standard deviation) ammonium-N, nitrate-N and phosphate-P concentrations in bores at the Haughton River site at Powerline, the Barratta Creek site at Northcote and the Burdekin River site at Clare between November 2011 and April 2013. Twelve samples were collected at each site, apart from RN 12000168 where eleven samples were collected.

5.2. Pesticides

The pesticides atrazine, its breakdown products desethyl atrazine (DEA) and desisopropyl atrazine (DIA), ametryn and propazin-2-hydroxy (from propazin) were detected at all sites, apart from Barratta Creek at Jerona Road (Table 8). Only atrazine and its breakdown products were detected at Barratta Creek at Jerona Road (Table 8). Simazine and metsulfuron-methyl were both detected at Barratta Creek at Northcote and the Burdekin River at Clare, and diuron, hexazinone, imidacloprid, metolachlor, tebuthiuron, 2,4-D, acifluorfen, haloxyfop (acid), isoxaflutole, MCPA and triclopyr were only detected at the Barratta Creek site at Northcote (Table 8). Of all the pesticides measured only diuron and metolachlor were detected at concentrations above the ANZECC and ARMCANZ (2000) TVs (Figure 20). Diuron was measured at a concentration above the diuron Ecotoxicity Threshold Value[6] proposed by Smith et al. (in prep) at the bore furthest from the river (RN 11911175) in February 2013 (Figure 20). Neither diuron nor metolachlor were detected in concentrations above the Australian Drinking Water Guidelines (NHMRC and NRMMC 2011) of 20 and 300 µg/L respectively. Graphs of all pesticides detected are presented in Appendices 6 to 9.

The most commonly detected pesticides in the Haughton River site at Powerline were the breakdown products DEA and DIA, which were detected at all bores in the majority of months (Table 9). Atrazine was detected at the bore furthest from the river bank but still in the riparian transect (RN 11900232) in most months.

The detections of pesticides showed greater spatial variability at the Barratta Creek site at Northcote and distinct differences were found between the established bore on the edge of the cane field (RN 1191204) and the transect bores (Table 10). As with the Haughton River site at Powerline, DEA and DIA were detected in most months at the established bore (RN 1191204) (Table 10). The only other pesticide detected in the bore was atrazine, which was measured in two months (Table 10). In contrast, ametryn, atrazine, diuron, hexazinone, DEA, DIA and propazin-2-hydroxy were detected in at least one bore in the transect for the majority of months in the Barratta Creek site at Northcote (Table 10). Imidacloprid, metolachlor, simazine, tebuthiuron, 2,4-D, acifluorfen, haloxyfop (acid), isoxaflutole and MCPA were detected multiple times, and there was a single detection of metsulfuron-methyl (Table 10). In addition many of these pesticides were only detected in February to April 2013 (Appendix 6) during the monitored wet season.

Fewer pesticides were detected in the Burdekin River site at Clare (Table 11), and there was a high spatial variability between bores where pesticides occurred. DEA and DIA were detected in all months in the established bore in the horticulture field (RN 1200168) and the middle bore of the riparian transect (RN 12001397) (Table 11). Neither DEA nor DIA were detected at the transect bore furthest from the river bank (RN 12001398), but atrazine was detected in 7 of 12 samples at that site (Table 11). DEA was detected in 10 out of 12 samples in the bore closest to the river bank (RN 12001396), but DIA was not detected in any sample and atrazine in only one. This may reflect

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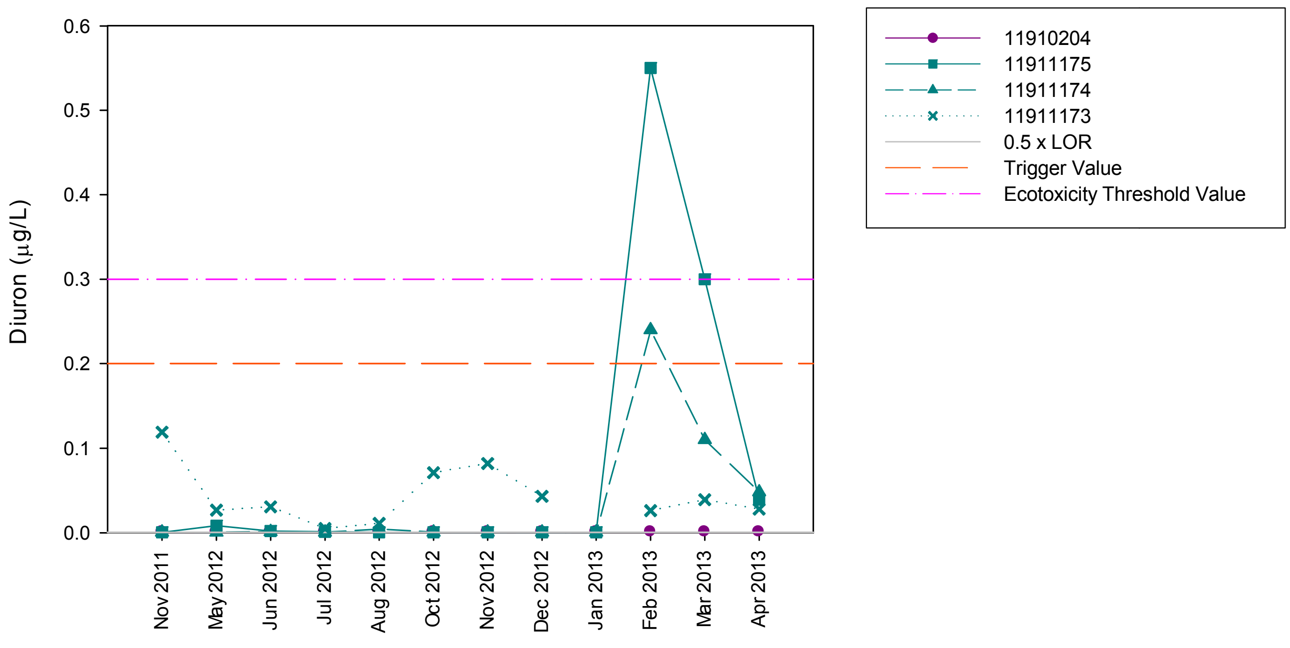
[6] The ecotoxicity threshold values (ETVs) were calculated using the proposed new method for deriving water quality guideline values for the revised ANZECC and ARMCANZ Water Quality Guidelines (Batley et al. 2013; Warne et al. in review). However, it should be noted, that although the ETVs were calculated using the same method as guideline values and should provide the same level of protection, they are termed Ecotoxicity Threshold Values because at the time of reporting they had not been nationally endorsed or have any official status.

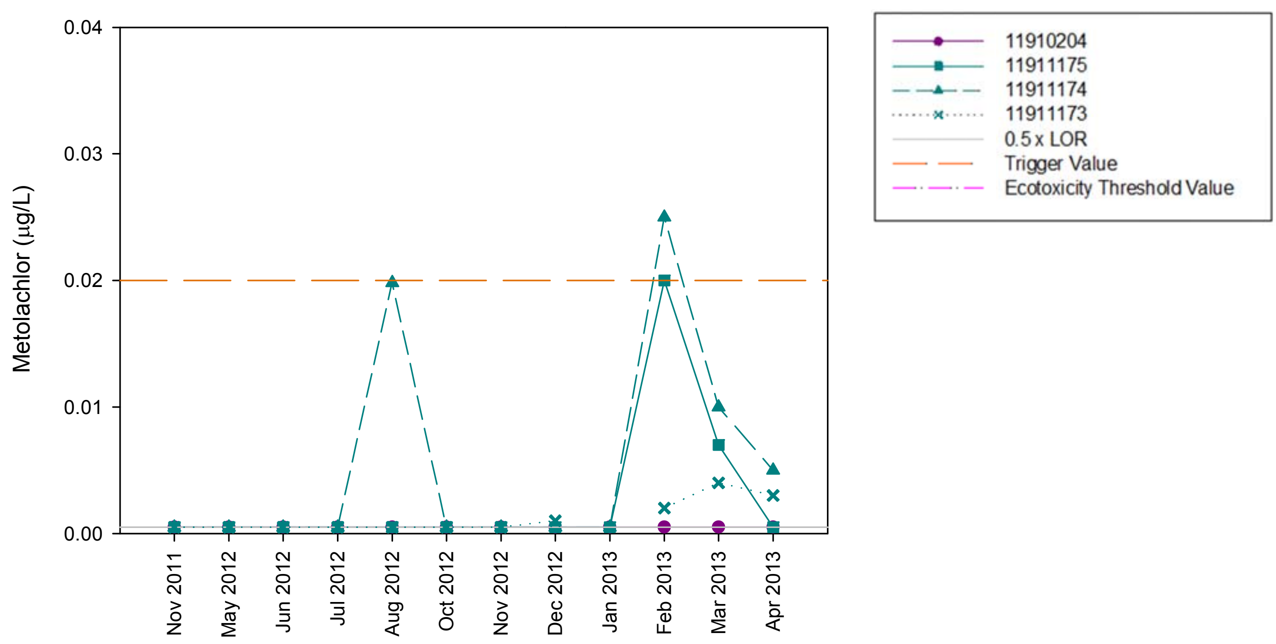
that both DEA and atrazine were generally detected at concentrations around the LOR, and there is a general trend in all bores that DIA is present in lower concentrations than DEA (Appendix 8). Atrazine, DEA and DIA were each only detected once at the Barratta Creek site at Jerona (Table 12).

Table 8 Summary of pesticides detected in the groundwater bores at the Haughton River site, Barratta Creek sites and the Burdekin River site.

Pesticide	Haughton River site at Powerline	Barratta site at Northcote	Burdekin site at Clare	Barratta Creek site at Jerona Road
Ametryn	x	x	x	
Atrazine	x	x	x	x
Desethylatrazine	x	x	x	x
Desisopropylatrazine	x	x	x	x
Diuron		x		
Hexazinone		x		
Imidacloprid		x		
Metolachlor		x		
Simazine		x	x	
Tebuthiuron		x		
2,4-D		x		
Acifluorfen		x		
Haloxyfop (acid)		x		
Isoxaflutole		x		
MCPA		x		
Metsulfuron-methyl		x	x	
Propazin-2-hydroxy	x	x	x	
Triclopyr		x		



(a)



(b)

Figure 20 Concentrations of (a) diuron and (b) metolachlor measured in four bores in the vicinity of Barratta Creek at Northcote. Note: Trigger Value refers to ANZECC and ARMCANZ (2000) trigger values and Ecotoxicity Threshold Value is a new value based on more recent ecotoxicological data (Smith et al. in prep).

Table 9 Summary of the number of months each pesticide was detected compared to the total number of months sampled and range of measured concentrations at Haughton River at Powerline. * Higher limit of reporting in May 2012 may underestimate number of detections.

Bore Number	RN 11900212		RN 11900232		RN 11900230		RN 11900229	
Pesticides	Months detected	Concentration range (µg/L)	Months detected	Concentration range (µg/L)	Months detected	Concentration range (µg/L)	Months detected	Concentration range (µg/L)
Ametryn	0/12	<0.001-<0.005	1/12	<0.001-0.001	0/11	<0.001-<0.005	0/12	<0.001-<0.005
Atrazine	0/12	<0.001-<0.005	10/12	<0.005-0.004	0/11	<0.001-<0.005	0/12	<0.001-<0.005
Desethylatrazine	12/12	0.045-0.082	12/12	0.1-0.167	11/11	0.038-0.069	12/12	0.001-0.114
Desisopropylatrazine	12/12	0.005-0.008	12/12	0.02-0.027	10/11*	<0.005*, 0.001-0.004	10/12	<0.001-0.006
Propazin-2-hydroxy	0/9	<0.001-<0.001	1/9	<0.001-<0.001	0/9	<0.001-<0.001	0/9	<0.001-<0.001

Table 10 Summary of the number of months each pesticide was detected compared to the total number of months sampled and range of measured concentrations at Barratta Creek at Northcote * Higher limit of reporting in May 2012 may underestimate number of detections.

Bore Number	RN 11910204		RN 11911175		RN 11911174		RN 11911173	
Pesticides	Months detected	Concentration range (µg/L)	Months detected	Concentration range (µg/L)	Months detected	Concentration range (µg/L)	Months detected	Concentration range (µg/L)
Ametryn	0/12	<0.001-<0.005	3/12	<0.001-0.067	8/12	<0.001-0.037	9/11	<0.005-0.006
Atrazine	2/12	<0.001-0.002	6/12	<0.001-2.1	10/12	<0.001-1.3	11/11	0.012-0.136
Desethylatrazine	12/12	0.012-0.022	5/12	<0.001-0.33	5/12	<0.001-0.0.17	11/11	0.010-0.063
Desisopropylatrazine	10/12*	<0.005-0.002*	4/12	<0.001-0.150	5/12	<0.001-0.081	10/11	<0.005-0.022
Diuron	0/12	<0.001-<0.005	6/12	<0.001-0.55	5/12	<0.001-0.240	11/11	0.005-0.119
Hexazinone	0/12	<0.001-<0.005	10/12	<0.005-0.011	3/12	<0.001-0.004	8/11	<0.001-0.005
Imidacloprid	0/12	<0.001-<0.005	3/12	<0.001- 0.048	4/12	<0.001-0.017	0/11	<0.001-<0.005
Metolachlor	0/12	<0.001-<0.005	2/12	<0.001- 0.020	4/12	<0.001-0.025	4/11	<0.001-0.004
Simazine	0/12	<0.001-<0.005	2/12	<0.001- 0.009	3/12	<0.001-0.005	0/11	<0.001-<0.005
Tebuthiuron	0/12	<0.001-<0.005	1/12	<0.001-0.001	6/12	<0.001-0.001	3/11	<0.001-<0.002
2,4-D	0/9	<0.004-<0.004	2/9	<0.004-0.290	1/9	<0.004-0.078	0/8	<0.004-<0.004
Acifluorfen	0/9	<0.004-<0.004	2/9	<0.004-0.088	1/9	<0.004-0.022	0/8	<0.004-<0.004
Haloxyfop (acid)	0/9	<0.004-<0.004	2/9	<0.004-0.026	1/9	<0.004-0.008	0/8	<0.004-<0.004
Isoxaflutole	0/9	<0.004-<0.004	3/9	<0.004-0.058	3/9	<0.004-0.068	3/8	<0.004-0.031
MCPA	0/9	<0.004-<0.004	2/9	<0.004-0.2	1/9	<0.004-0.044	0/8	<0.004-<0.004
Metsulfuron-methyl	0/8	<0.001-<0.001	1/8	<0.001-0.002	0/8	<0.001-<0.001	0/7	<0.001-<0.001
Propazin-2-hydroxy	0/9	<0.001-<0.001	2/9	<0.001-0.012	3/9	<0.001-0.003	8/8	0.006-0.015
Triclopyr	0/9	<0.004-<0.004	1/9	<0.004-0.004	0/9	<0.004-<0.004	0/8	<0.004-<0.004

Table 11 Summary of the number of months each pesticide was detected compared to the total number of months sampled and range of measured concentrations at Burdekin River at Clare. * Higher limit of reporting in May 2012 may underestimate number of detections.

Bore Number	RN 12000168		RN 12001398		RN 12001397		RN 12001396	
Pesticides	Months detected	Concentration range (µg/L)	Months detected	Concentration range (µg/L)	Months detected	Concentration range (µg/L)	Months detected	Concentration range (µg/L)
Ametryn	0/11	<0.001-<0.005	0/12	<0.001-<0.005	0/12	<0.001-<0.005	1/12	<0.001-0.001
Atrazine	0/11	<0.001-<0.005	7/12	<0.001-0.018	0/12	<0.001-<0.005	1/12	<0.001-0.001
Desethylatrazine	11/11	0.060-0.327	0/12	<0.001-<0.005	12/12	0.049-0.091	10/12*	<0.005-0.003
Desisopropylatrazine	11/11	0.016-0.029	0/12	<0.001-<0.005	12/12	0.005-0.009	0/12	<0.001-<0.005
Simazine	1/11	<0.001-0.001	0/12	<0.001-<0.005	0/12	<0.001-<0.005	1/12	<0.001-0.002
Metsulfuron Methyl	1/8	<0.001-0.003	0/8	<0.001-<0.001	0/8	<0.001-<0.001	0/8	<0.001-<0.001
Propazin-2-hydroxy	0/9	<0.001-<0.001	0/9	<0.001-<0.001	0/9	<0.001-<0.001	1/9	<0.001-0.002

Table 12 Summary of the number of months each pesticide was detected compared to the total number of months sampled and range of measured concentrations at Barratta Creek at Jerona.

Bore Number	RN 11910887B	
Pesticides	Months detected	Range
Atrazine*	1/11	<0.001-0.002
Desethylatrazine	1/11	<0.005-0.047
Desisopropylatrazine	1/11	<0.001-0.005

* Note: detected in deeper pipe (RN 11910887A) in November 2012 which was accidently sampled.

The desethylatrazine to atrazine ratio (DAR) has been used to assess relative residence times in soils (Jayachandran et al. 1994 cited in Baskaran et al. 2001). As DEA is more water soluble than atrazine, and soil micro-organisms convert atrazine to DEA, a DAR >1 indicates that atrazine has had a relatively long residence time in the soil and DEA concentrations have had time to accumulate (Jayachandran et al. 1994 cited in Baskaran et al. 2001). Conversely, a DAR <1 indicates that atrazine has rapidly leached through soil before conversion to DEA could occur (Jayachandran et al. 1994 cited in Baskaran et al. 2001). The DAR ratios calculated from the data collected at the four sites indicate that two different processes are occurring at the monitored sites. The mean DAR for all bores in the Haughton River site at Powerline was greater than 1 (ranging from 36 to 58) (Figure 21). In the two bores at the Burdekin River at Clare site where the majority of concentrations of DEA was generally higher than the LOR (RN 1200168 and RN 12001397), large DARs also occurred (Figure 21). For the other two bores the DAR was essentially 1 (Figure 21). This latter result is an artefact of the concentrations of both chemicals being around the LOR. The single significant detection of DEA at the Barratta Creek site at Jerona resulted in a high DAR (i.e. 47), indicating that atrazine has had a long soil residence time. However, a different situation occurred at the Barratta Creek site at Northcote. Whilst the DAR for the established bore (RN 1910204) indicated that atrazine had been resident in the for a long time, the DARs calculated for the samples collected from the bores in the riparian transect were all less than 1, indicating atrazine had a short residence time in the soil. The implications of these DAR values will be discussed in the following section.

6. Flux of Pesticides through the Riparian Zone in Barratta Creek

It has been noted previously that many of the 18 pesticides detected in the groundwater of the riparian transect at the Barratta Creek site at Northcote were detected following the wet period at the end of January 2013 (detected in groundwater samples collected between February and April 2013), particularly in the two bores in the transect furthest away from the creek (RN11911175 and RN 1191174). Between 24 and 25 January 2013 the river height peaked at approximately 18 m (Figure 22). A comparison was made between the pesticides detected in the groundwater bore (RN 1191175) following this flood event and those detected in the surface waters in Barratta Creek during the flood (Table 13). Of the 18 pesticides detected in the groundwater bores, thirteen were also detected in the surface water between 24 and 27 January 2013 (Table 15). Of the five pesticides detected in the groundwater and not the surface water, all were measured in the groundwater at concentrations lower than the LOR for the surface water samples (Table 15). In addition, the concentration of pesticides in RN 11911175 went from being below the LOR prior to the flood to concentrations in the same order of magnitude of those measured in the creek during the flood period (Table 15). The DARs measured in the surface waters (Table 14) were less than 1, as were the DARs measured in the groundwaters subsequent to flooding (Figure 21). The conductivity in water in these bores in February 2013 also decreased to levels similar to that found in the creek at the time (100-250 µS/cm between 24 and 27 January 2013, time of flood peak (Figure 13a). Elevated concentrations of phosphate, DOC and nitrate were also noted at this time (Appendix 3). This, combined with the evidence from the DAR ratios, indicate lateral exchange of surface water may be occurring at this site in response to flood events. The same pattern of contamination was generally noted at RN 11911174, whereas it was not noted in the bore closest to the creek (RN 11911173) (see Appendix 3 and 7). RN 11911173 is strongly connected to the creek (Figure 11).

Rassam et al. (2008 cited in Hunter (2012)) noted that temporary storage of stream water in banks or riparian zones occurs when rising stream waters move into banks and riparian zones and drain back into the creek as they recede. It has been suggested that lateral exchange may be dominant over the regional inputs in large river floodplains, particularly in semi-arid climates where large surface water levels occur (Lamontagne et al. 2006 and references cited within). Although Barratta Creek at Northcote is a small waterway, large variations in water height do occur for short periods of time (Figure 11). It appears that lateral exchange is the dominant process for temporary contamination of the aquifer with pesticides and possibly phosphate. In this case, based on the pesticides concentrations, the drainage back to the creek occurs over a period of several months, and may contribute to the pesticide concentrations in the creek during ambient conditions. During the major part of the year, the water table height is elevated well above the Barratta Creek height (Figure 22a) and therefore the water table will be flowing toward the creek. However during the flood period, the river height was elevated above the water table height at RN 191173 and RN 1191174, which would indicate that contamination of these bores with river water is possible during the flood (Figure 22b). Hunter (2012) does not consider these to be groundwater process as they arise from the infiltration of surface flow and associated links to land management. This lateral exchange does not appear to be occurring at either the Haughton River at Powerline or Burdekin River at Clare sites, however monitoring over the major wet season (December 2011 - April 2012) was not undertaken, where river heights at these sites were much larger than those in January 2013 (Figure 10 and Figure 12) and a greater hydraulic connectivity is likely to have occurred. These rivers are much larger than the Barratta Creek. It is not possible to rule out contamination of the aquifers due to deep drainage following the heavy rainfall in the area, as deep drainage and a rising water table is a significant problem for the BHWSS area. A combination of processes may be occurring.

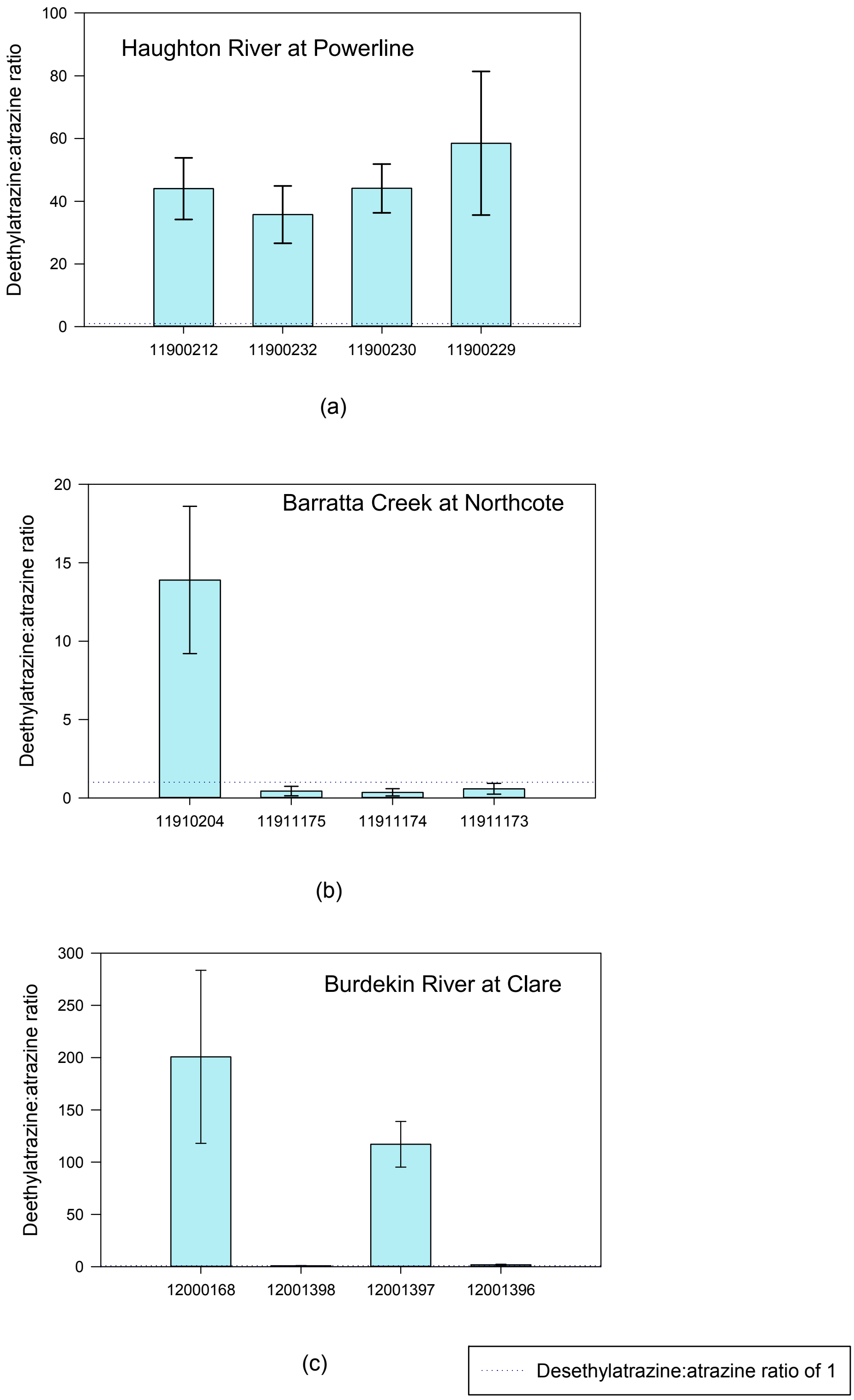


Figure 21 Calculated mean (± standard deviation) desethyl atrazine to atrazine (DAR) ratios for bores from (a) the Haughton River site at Powerline, (b) the Barratta Creek site at Northcote and (c)the Burdekin River site at Clare. The single value at the Barratta Creek site at Jerona gave a DAR of 47. Where a results was were reported as below the limit of reporting, the limit of reporting was used for the calculation. Star indicates all results were around the limit of reporting and so cannot be fully assessed.

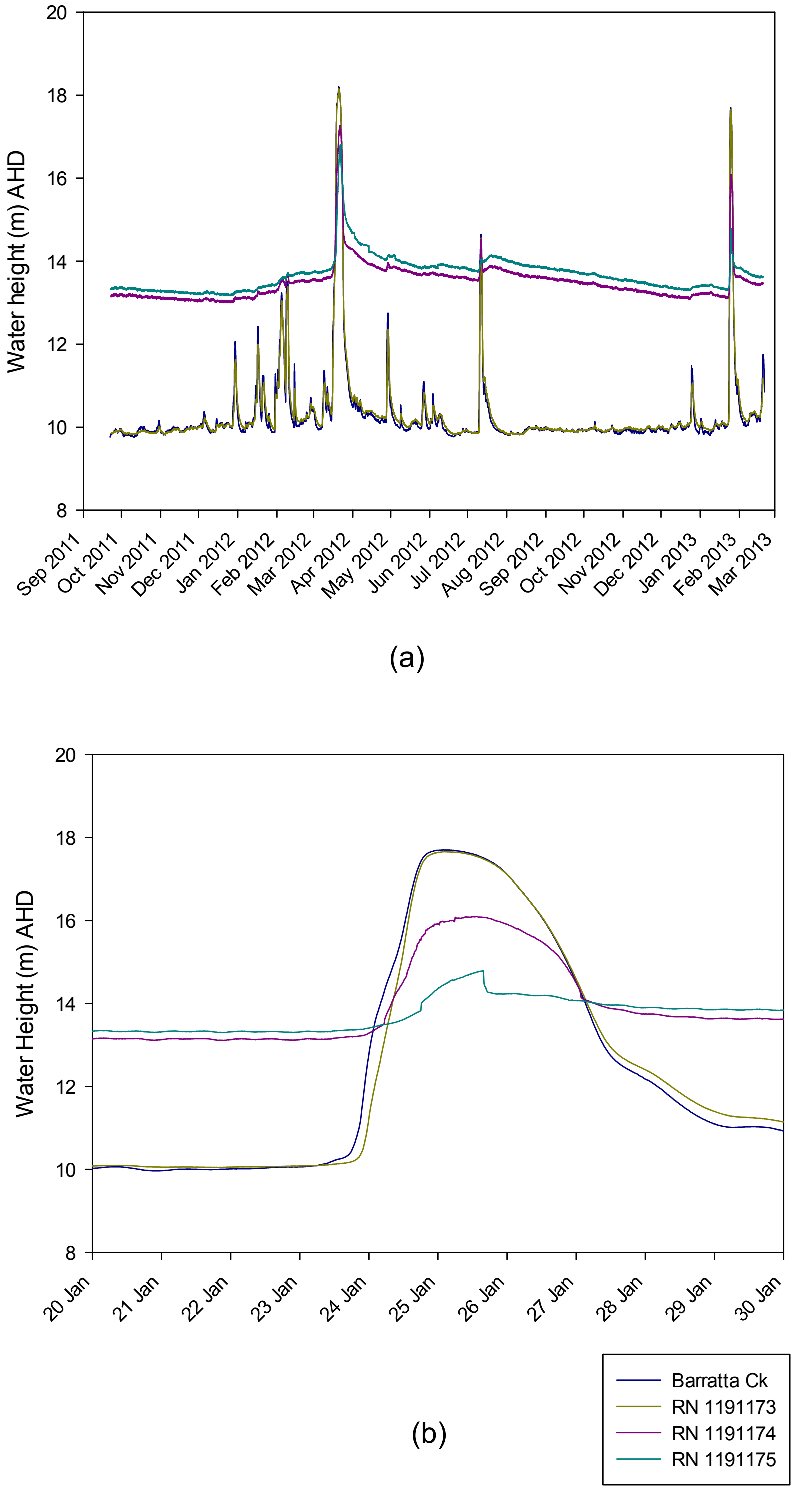


Figure 22 Comparison of (a) water heights of the transect bores in the Barratta Creek at Northcote site compared to Barratta Creek height for the sampling period (b) water heights during flood period.

Table 13 Summary of pesticides detected in surface waters of Barratta Creek at Northcote during the flood peak (24 to 27 January) and in groundwater (RN 1191175) between February and April 2013 in the riparian transect bores.

Pesticide	Detected in groundwater	Detected in surface waters
Ametryn	x	x
Atrazine	x	x
Desethylatrazine	x	x
Desisopropylatrazine	x	x
Diuron	x	x
Hexazinone	x	x
Imidacloprid	x	x
Metolachlor	x	xx
Simazine	x	x
Tebuthiuron*	x	xx
2,4-D	x	x
Acifluorfen	x	x
Haloxyfop (acid)	x	x
Isoxaflutole	x	x
MCPA	x	x
Metsulfuron-methyl *	x	xx
Propazin-2-hydroxy *	x	xx
Triclopyr*	x	xx

Note: x indicates the pesticide has been detected, xx means the pesticide was not detected in surface waters between 24 and 27 January 2013 but was detected at other times, * indicates that the limit of reporting for surface waters was higher than for groundwater and the groundwater concentrations measured at concentrations lower than the surface water limit of reporting.

Table 14 Summary of desethylatrazine to atrazine (DAR) ratios for surface water samples collected in Barratta Creek at Northcote during flood period of 24 to 27 January.

Date	DAR
24/01/2013 03:30 PM	0.08
25/01/2013 07:45 AM	0.08
25/01/2013 04:00 PM	0.10
27/01/2013 08:20 AM	0.10

Table 15 Concentrations of pesticides detected in groundwater in bores RN 11911175 before and after the January 2013 flood. Concentrations of pesticides in surface waters of Barratta Creek during the flood peak of 24 to 27 January and in groundwater between February and April 2013 in the transect bores located in the riparian zone.

Analyte	Pesticide concentrations (µg/L)							
	Month groundwater samples collected					Date surface water samples collected		
	Oct 2012	Nov 2012	Dec 2012	Jan 2013	Feb 2013	24/01/2013 pm	25/01/2013 am	25/01/2013 pm
2,4-D	<0.004	<0.004	<0.004	<0.004	0.29	0.09	0.1	0.28
Acifluorfen	<0.004	<0.004	<0.004	<0.004	0.088	0.19	0.18	0.15
Ametryn	<0.001	<0.001	<0.001	<0.001	0.067	0.05	0.04	0.05
Atrazine	<0.001	<0.001	<0.001	<0.001	2.1	7.84	5.89	3.52
Desethylatrazine	<0.001	<0.001	<0.001	<0.001	0.33	0.61	0.5	0.37
Desisopropylatrazine	<0.001	<0.001	<0.001	<0.001	0.15	0.27	0.23	0.18
Diuron	<0.001	<0.001	<0.001	<0.001	0.55	1.46	1.09	0.79
Haloxyfop (acid)	<0.004	<0.004	<0.004	<0.004	0.026	0.02	0.02	0.02
Hexazinone	0.001	0.002	0.001	0.002	0.011	0.02	0.01	0.01
Imidacloprid	<0.001	<0.001	<0.001	<0.001	0.048	0.31	0.35	0.24
Isoxaflutole	<0.004	<0.004	<0.004	<0.004	0.016	0.04	0.04	0.1
MCPA	<0.004	<0.004	<0.004	<0.004	0.2	0.01	0.01	0.02
Metolachlor	<0.001	<0.001	<0.001	<0.001	0.02	<0.01	<0.01	<0.01
Metsulfuron-methyl	<0.001	<0.001	<0.001	<0.001	0.002	<0.01	<0.01	<0.01
Propazin-2-hydroxy	<0.001	<0.001	<0.001	<0.001	0.012	0.03	0.02	<0.01
Simazine	<0.001	<0.001	<0.001	<0.001	0.009	<0.01	<0.01	<0.01
Tebuthiuron	<0.001	<0.001	<0.001	<0.001	0.001	<0.01	<0.01	<0.01
Triclopyr	<0.001	<0.001	<0.001	<0.001	0.004	<0.01	<0.01	<0.01

7. Estimation of contribution of loads from groundwater

The contribution of groundwater to the overall loads measured at end of system sites monitored by the Great Barrier Reef Catchment Loads Monitoring Program (GBRCLMP) were calculated where data were available for end of system sites (Barratta and Burdekin). The groundwater discharge from each river system was estimated by Cook et al. (2011) using geochemical tracers and modelling at the end of May 2011, i.e. during the dry season. There is an inherent uncertainty in the estimates, with Cook et al. (2011) indicating uncertainty of ±50% or higher. A range of loads were calculated using this uncertainty value. The calculated mean from a single site within each catchment studied in this survey was used, and hence there will be a high degree of uncertainty in the groundwater loads. None the less, the estimates provide some context for understanding the contribution of contaminants in groundwater to the overall loads reaching the GBR.

The mean concentration of each analyte was calculated for the bore closest to the river and closest to the estimated discharge zone at each site (Table 16, Table 17 and Table 18). The groundwater loads were then calculated by multiplying the mean concentration of each analyte by the average daily discharge volume given (Cook et al. 2011) and then converting the number to an annual load. These numbers were then compared to loads provided by the GBRCLMP (Table 19, Table 20 and Table 21). The estimated nitrate and phosphate groundwater loads were less than 1% of the total loads calculated to arise from these sites, apart from nitrate-N at the Burdekin at Clare which was approximately 6.5% (with a range based on error estimated by Cook (2011) of 3.25–9.74%) (Table 19). However, the potential ammonium load was significant, being calculated as 399% (with an estimate range of 199–598%) at Barratta Creek and 30% (with an estimate range of 15–44%) at Burdekin River (Table 19). Ammonium is quickly transformed back to nitrate under oxygenating conditions (Korom 1992 cited in Hunter 2012), and this may account for the discrepancy between results in the ammonium loads. As noted previously, it is thought that the ammonium in the riparian zone is produced by the decomposition of organic matter within the riparian zone, rather than being from nitrate moving from agricultural lands and being transformed to ammonium. Total loads are not available for the Haughton site so it is not possible to assess the contribution of groundwater to these loads.

Groundwater also appeared to contribute little to the overall pesticides loads (Table 20 and Table 21). All pesticides, with the exception of hexazinone, propazin-2-hydroxy and tebuthiuron, were estimated to contribute less than 2% to the overall loads at Barratta Creek. It was estimated that groundwater contributed approximately 45% of the tebuthiuron load for Barratta Creek (with a range of 22–68%), 24.5% of propazine-2-hydroxy (estimated range 12.3–36.8%) and 4.5% of hexazinone (estimated range 2.22–6.67%). All the measurements of tebuthiuron were at the limit of reporting and the calculated loads may reflect uncertainties at low concentrations. Tebuthiuron is not used in the sugar industry and it is thought that its presence in the area is due to irrigation water being taken from the Burdekin River, which receives the tebuthiuron from the grazing industry further up the catchment. It was estimated groundwater contributed 4.66% (estimated range of 2.33–6.99 %) to the overall loads of ametryn in the Burdekin River, but less than 1% for other pesticides (Table 21).

Table 16 Estimated groundwater discharge (from Cook et al. 2011) for each river catchment and the mean concentration of nutrients from the bore closest to the river at each site.

	Estimated Volume (ML/day) from Cook (2011)	Mean ammonium nitrogen as N (mg/L)	Standard Deviation	Mean oxidised nitrogen as N (mg/L)	Standard Deviation	Mean Phosphate phosphorus as P (mg/L)	Standard Deviation
Barratta (RN 1191173)	56	1.054	0.154	0.011	0.007	0.0005	0.0001
Burdekin (RN 12001396)	248	0.123	0.014	0.54	0.16	0.006	0.010

Table 17 Mean and standard deviation of concentration of pesticides from the bore closest to Barratta Creek (RN 1191173).

	Ametryn (µg/L)	Atrazine (µg/L)	Desethyl Atrazine (µg/L)	Desisopropyl Atrazine (µg/L)	Diuron (µg/L)	Hexazinone (µg/L)	Metolachlor (µg/L)	Tebuthiuron (µg/L)	Isoxaflutole (µg/L)	Propazin-2-hydroxy (µg/L)
mean	0.003	0.061	0.025	0.010	0.044	0.002	0.002	0.001	0.008	0.010
std dev	0.0011	0.040	0.016	0.0060	0.034	0.0016	0.0013	0.0008	0.011	0.0033

Table 18 Mean and standard deviation of the concentration of pesticides from the bore closest to Burdekin River (RN 12001396).

	Ametryn (µg/L)	Atrazine (µg/L)	Desethyl Atrazine (µg/L)	Propazin-2-hydroxy (µg/L)	Simazine (µg/L)
mean	0.001	0.001	0.002	0.001	0.001
std dev	0.0008	0.0008	0.0008	0.0005	0.0008

Table 19 Nutrient loads from groundwater from each river catchment, from the Great Barrier Reef Catchment Loads Monitoring Program (GBRCLMP) end of system sites and the percentage contribution of groundwater to the total load.

		Ammonium nitrogen as N	Ammonium nitrogen as N range based on ± 50% error cited by Cooke (2011)	Oxidised nitrogen as N	Oxidised nitrogen as N range based on ± 50% error cited by Cooke (2011)	Phosphate as P	Phosphate as P range based on ± 50% error cited by Cooke (2011)
Barratta	Estimate Loads GW (t/yr)	22 ± 3	11 - 32	0.22 ± 0.15	0.11 - 0.33	0.011 ± 0.003	0.005 - 0.015
	Loads GBRCLMP (t/yr)	5.4		88		10	
	GW loads as a % of total loads	399 ± 58	199-598	0.25 ± 0.17	0.13 - 0.38	0.11 ± 0.02	0.05- 0.15
Burdekin	Estimate Loads GW (t/yr)	11 ± 1	6 - 17	49 ± 14.47	25 - 74	0.57 ± 0.95	0.29 – 0.86
	Loads GBRCLMP (t/yr)	38		760		360	
	GW loads as a % of total loads	30 ± 3	15 - 44	6.49 ± 1.90	3.25 - 9.74	0.16 ± 0.26	0.08 - 0.24

Table 20 Pesticide loads from groundwater at Barratta Creek at Northcote from the Great Barrier Reef Catchment Loads Monitoring Program (GBRCLMP) end of system site and the percentage contribution of groundwater to the total load.

	Estimated loads groundwater (kg) (± standard deviation)	GBRCLMP loads (kg)	GW loads as a % of GBRCLMP loads	Range of groundwater loads as a % of GBRCLMP loads based ± 50 % error based on Cook 2011
Ametryn	0.069 ± 0.023	13.0	0.53 ± 0.18	0.27 - 0.80
Atrazine	1.25 ± 0.81	440.0	0.28 ± 0.18	0.14 - 0.43
Desethylatrazine	0.52 ± 0.33	47.0	1.10 ± 0.71	0.55 - 1.65
Desisopropylatrazine	0.20 ± 0.12	20.0	1.01 ± 0.61	0.50 - 1.51
Diuron	0.89 ± 0.69	80.0	1.12 ± 0.87	0.56 - 1.68
Hexazinone	0.049 ± 0.032	1.1	4.44 ± 2.92	2.22 - 6.67
Metolachlor	0.033 ± 0.026	16.0	0.20 ± 0.16	0.10 -0 .30
Tebuthiuron	0.022 ± 0.017	0.0	45.5 ± 34.67	22.75 - 68.26
Isoxaflutole	0.17 ± 0.22	21.0	0.79 ± 1.05	0.40 - 1.17
Propazin-2-hydroxy	0.20 ± 0.068	0.8	24.5 ± 8.45	12.3 - 36.8

Table 21 Pesticide loads from groundwater at Burdekin River at Clare from the Great Barrier Reef Catchment Loads Monitoring Program (GBRCLMP) end of system site and the percentage contribution of groundwater to the total load.

	Estimated loads groundwater (kg) (± standard deviation)	GBRCLMP loads (kg)	GW loads as a % of GBRCLMP loads	Range of GW loads as a % of GBRCLMP loads based on Cook 2011
Ametryn*	0.079 ± 0.070	1.7	4.66 ± 4.11	2.33 - 6.99
Atrazine*	0.079 ± 0.070	180.0	0.044 ± 0.039	0.02 - 0.07
Desethyl Atrazine	0.17 ± 0.068	32.0	0.54 ± 0.21	0.27 - 0.82
Propazin-2-hydroxy*	0.060 ± 0.045	NC	NC	NC
Simazine*	0.087 ± 0.076	NC	NC	NC

Note: * estimated groundwater loads based on a detection in a single month. Half the limit of reporting was used to estimate concentrations in other months. NC means not calculated as either not detected in surface waters or limited data.

8. Summary and conclusions

It was clear that the concentration of nitrate and phosphorous decreased through the riparian zone at Barratta Creek at Northcote and the Burdekin River at Clare, and the concentration of ammonium increased towards the river, particularly at Barratta Creek at Northcote. Geochemical conditions present at these sites indicate that denitrification may be occurring and removing nitrate from the system as nitrogen gas, with the ammonium possibly being a product of the decomposition of organic material within the riparian zone. This pattern was not observed at the Haughton River at Powerline, where there was little change in concentration of nitrate and phosphate through the riparian zone. The reason for this is not fully understood, although there appears to be almost no hydraulic connectivity with the Haughton River in this area.

Concentrations of pesticides were present but were generally low in the groundwater at all sites, apart from the transect area of the Barratta Creek at Northcote site. This site showed a large temporal variation in pesticide concentration with a peak in concentrations subsequent to a flood event. This, along with a decrease in specific conductivity that reflected the surface water specific conductivity, indicated that lateral exchange with the creek's surface water was occurring. The pesticide concentrations decreased in these bores over a period of a couple of months post flood.

Estimations indicate that annual groundwater contribution to the overall loads of both pesticide and nutrient contaminants travelling to the reef through the riparian zone are relatively small. This was not the case for ammonium, with estimations indicating that groundwater contributes significantly to the overall ammonium loads. Based on the geochemical conditions, it is likely that ammonium is being produced within the riparian system rather than via transformation of nitrate from farm runoff. Further work should be undertaken to fully confirm this conclusion.

It should be highlighted that this work focussed on understanding the transport and transformations of groundwater contaminants through the riparian zone in the Burdekin Haughton Water Supply Scheme. The Burdekin River delta zone is a different system and results from this study cannot be extrapolated to that area. In addition, groundwater is extracted and used for irrigation in the Burdekin River delta zone, and the proportion of contamination from this water (which may be considered surface water once extracted) has not been assessed.

9. Recommended future work

- In the lower Burdekin, improved understanding of groundwater discharge loads is now limited by the very limited understanding of the water flow, which may vary substantially over time. Further radon/tracer studies and groundwater modelling should be undertaken.
- Evaluation of groundwater flow into drains and the potential for recycling of contaminants through irrigation should be further investigated.
- Looking at the GBR catchments more broadly, and the coastal sugar cane lands in particular, there is considerable potential for fairly rapid groundwater discharge and contaminant transport to constructed drains and then into streams without the geochemical transformation that occurs in riparian zones. Cane lands are known to have high rates of deep drainage and temporary elevated water tables which the drains are intended to lower. There are many 1000's of km of these drains. Loads of contaminants via these drains should be monitored. There is also a need to model this pathway and possible management practices, which is currently not possible due to a lack of data.

10. 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.

Barnes M, Marvanek S and Miller R. 2005. *Lower Burdekin ground water–statistical analysis of salinity & nitrate levels*. CSIRO Mathematical and Information Sciences Report 04/104, Adelaide, p. 57.

Bauld J. 1996. *Groundwater quality: human impact on a hidden resource*. In: Hydrology and Water Resources Symposium (23rd, 1996, Hobart, Tasmania). Hydrology and Water Resources Symposium 1996: Water and the Environment; Preprints of Papers. Barton, ACT: Institution of Engineers, Australia, 1996: p. 143–147. National conference publication (Institution of Engineers, Australia); no. 96/05.

Brodie J, Binney J, Fabricius K, Gordon I, Hoegh-Guldberg O, Hunter H, O'Reagain P, Pearson R, Quirk M, Thorburn P, Waterhouse J, Webster I and Wilkinson S. 2008. *Synthesis of evidence to support the Scientific Consensus Statement on Water Quality in the Great Barrier Reef*. Reef Water Quality Protection Plan Secretariat, Department of Premier and Cabinet, Brisbane.

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), vol. 8, 187–215.

Kroon F, Turner R, Smith, R, Warne M, Hunter H, Bartely R, Wilkinson S, Lewis S, Waters, D and Carroll C. *Sources of sediment, nutrients, pesticides and other pollutants in the Great Barrier Reef Catchment*. In: Synthesis of evidence to support the Reef Water Quality Scientific

Consensus Statement 2013. Department of the Premier and Cabinet, Queensland Government, Brisbane. http://www.reefplan.qld.gov.au/about/scientific-consensus-statement/assets/scsu-chapter-4-sources-of-pollutants.pdf

Brusch W and Nilsson B. 1993. Nitrate transformation and water movement in a wetland area, *Hydrobiologia*, vol. 251, p. 103–111.

Cook PG, Lamontagne S, Stieglitz T, Cranswick R and Hancock G. 2011. *A re-evaluation of groundwater discharge from the Burdekin foodplain aquifer using geochemical tracers*. National Centre for Groundwater Research and Training, Flinders University, Adelaide, p. 105.

Cooper AB. 1990. Nitrate depletion in the riparian zone and stream channel of a small headwater catchment. *Hydrobiologia*, vol. 202, p. 13–26.

DEHP (Department of Environment and Heritage Protection). 2009. *Queensland Water Quality Guidelines*, Version 3, ISBN 978-0-9806986-0-2.

Foy Z and Bajracharya. K. 2012. *Development of a hydrological modelling toolkit to support sustainable development of the Lower Burdekin groundwater system:Instuctional solute transport model of the Lower Burdekin aquifer*, Department of Science, Information Technology, Innovation and the Arts, Brisbane.

Haycock NE and Burt TP. 1993. *The sensitivity of rivers to nitrate leaching: The effectiveness of near-stream land as a nutrient retention zone*. p. 261–272. *In* D.S.G Thomas and R.J Allison (ed.) *Landscape sensitivity*. John Wiley and Sons, New York.

Haycock NE and Pinay G. 1993. Groundwater nitrate dynamics in grass and poplar vegetated riparian buffer strips during the winter. *Journal of Environmental Quality*, vol. 22, p. 273–278.

Hill AR. 1996. Nitrate removal in stream riparian zones. *Journal of Environmental Quality*, vol. 25, no. 4, p. 743–755.

Hunter HM. 2012. Nutrients and herbicides in groundwater flows to the Great Barrier Reef lagoon: processes, fluxes and links to on-farm management. Australia. ISBN: 978-1-7423-0969. Available at: [http://www.qld.gov.au/environment/assets/documents/agriculture/sustainable-farming/reef/rp51c-grounderwater-report.pdf]

Jayachandran K, Steinheimer TR, Somasundara L, Moorman TB, Kanwar RS and Coats JR. 1994. Occurrence of atrazine and degradates as contaminants of subsurface drainage and shallow groundwater. *Journal of Environmental Quality,* vol. 23, p. 311–319.

Keating BA, Bauld J, Hillier J, Ellis R, Weier KL, Sunners F and Connell D. 1996. *Leaching of nutrients and pesticides to Queensland groundwaters*. In: Hunter HM, Eyles AG, Rayment GE (Eds.), Downstream Effects of Land-use. Department of Natural Resources, Brisbane, p. 151–163.

Klok JA and Ham GJ. 2004. *A pilot study into pesticides and the Burdekin delta aquifer system*. Proceedings of Australian Society of Sugar Cane Technologists, vol. 26.

Korom SF. 1992. Natural denitrification in the saturated zone: A review, *Water Resources Research*, vol. 28, no. 6, p. 1657–1668.

Lamontagne S, Herczeg AL, Dighton JC, Jiwan JS and Pritchard JL. 2005. Pattern in groundwater nitrogen concentration in the floodplain of a subtropical stream (Wollombi Brook, New South Wales). *Biogeochemistry*, vol. 72, p. 169–190.

Lamontagne S, Leaney FW and Herczeg AL. 2006. Pattern in groundwater nitrogen concentration in the riparian zone of a large semi-arid river (River Murray, Australia). *River Research and Applications*, vol. 22, p. 39–54.

Lenahan MJ. 2012. *Development of a hydrological modelling toolkit to support sustainable development of the Lower Burdekin groundwater system: Geochemical assessment and reactive transport modelling of nitrogen dynamics in the lower Burdekin coastal plain aquifer*, Department of Science, Information Technology, Innovation and the Arts, Brisbane.

McMahon GA, Reading L, Foy Z, Wang J, Bajracharya. K, Corbett N, Gallager M, Lenahan MJ and Gurieff L. 2012. *Development of a hydrological modelling toolkit to support sustainable development of the Lower Burdekin groundwater system: Conceptualisation of the Lower Burdekin aquifer*, Department of Science, Information Technology, Innovation and the Arts, Brisbane.

Narayan KA, Schleeberger C, Charlesworth PB and Bristow KL. 2003. *Effects of groundwater pumping on saltwater intrusion in the lower Burdekin delta, north Queensland*. MODSIM 2003 International Congress on Modelling and Simulation, vol. 2, p. 212–217. Modelling and Simulation Society of Australia and New Zealand, July 2003.

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.

Petheram C, Bristow KL and Nelson PN. 2008. Understanding and managing groundwater and salinity in a tropical conjunctive water use irrigation district. *Agricultural Water Management*, vol. 95, p. 1167–1179.

Rassam DW, Pagendam DE and Hunter HM. 2008. Conceptualisation and application of models for groundwater-surface water interactions and nitrate attenuation potential in riparian zones. *Environmental Modelling and Software*, vol. 23, pp. 859–875.

Reading L, Wang J, Lenahan MJ, Gallager, M and Foy Z. 2012. *Development of a hydrological modelling toolkit to support sustainable development of the Lower Burdekin groundwater system: Review of Modelling Methods*, Department of Science, Information Technology, Innovation and the Arts, Brisbane.

SKM (Sinclair Knight Merz). 2009. *Groundwater science plan – A science plan for the sustainable management of the Lower Burdekin.* Sinclair Knight Merz Pty Ltd, Melbourne.

Shaw MS, Silburn DS, Lenahan M and Harris M. 2012. *Pesticides in groundwater in the Lower Burdekin floodplain*. Department of Environment and Resource Management, Queensland Government, Brisbane. ISBN: 978-1-7423-0953.

Smith R, Warne M.St.J., Delaney K, Turner R, Seery C, Pradella N, Vardy S, Rogers B, Arango C, Edge K, Julli, M. (in prep). Proposed guideline values for six priority pesticides of the Great Barrier Reef and its adjacent catchments.

Stookey LL. 1970. Ferrozine – a new spectrophotometric reagent for iron. *Analytical Chemistry*, vol. 42, p. 779–781.

Thayalakumaran T, Bristow KL, Charlesworth PB and Fass T. 2008. Geochemical conditions in groundwater systems: Implications for the attenuation of agricultural nitrate. *Agricultural Water Management*, vol. 95, no. 2, p. 103–115.

Thomasson AJ, Bouma J and Leith H (Eds.). 1991. *Soil and Groundwater Research Report. II. Nitrate in Soils.* EUR13501 Office for Official Publications of the European Communities, Luxembourg, p. 544.

Wang J, Bajracharya. K, Gallager, M and Corbett N. 2012. *Development of a hydrological modelling toolkit to support sustainable development of the Lower Burdekin groundwater system: Groundwater flow modelling of the Lower Burdekin aquifer*, Department of Science, Information Technology, Innovation and the Arts, Brisbane.

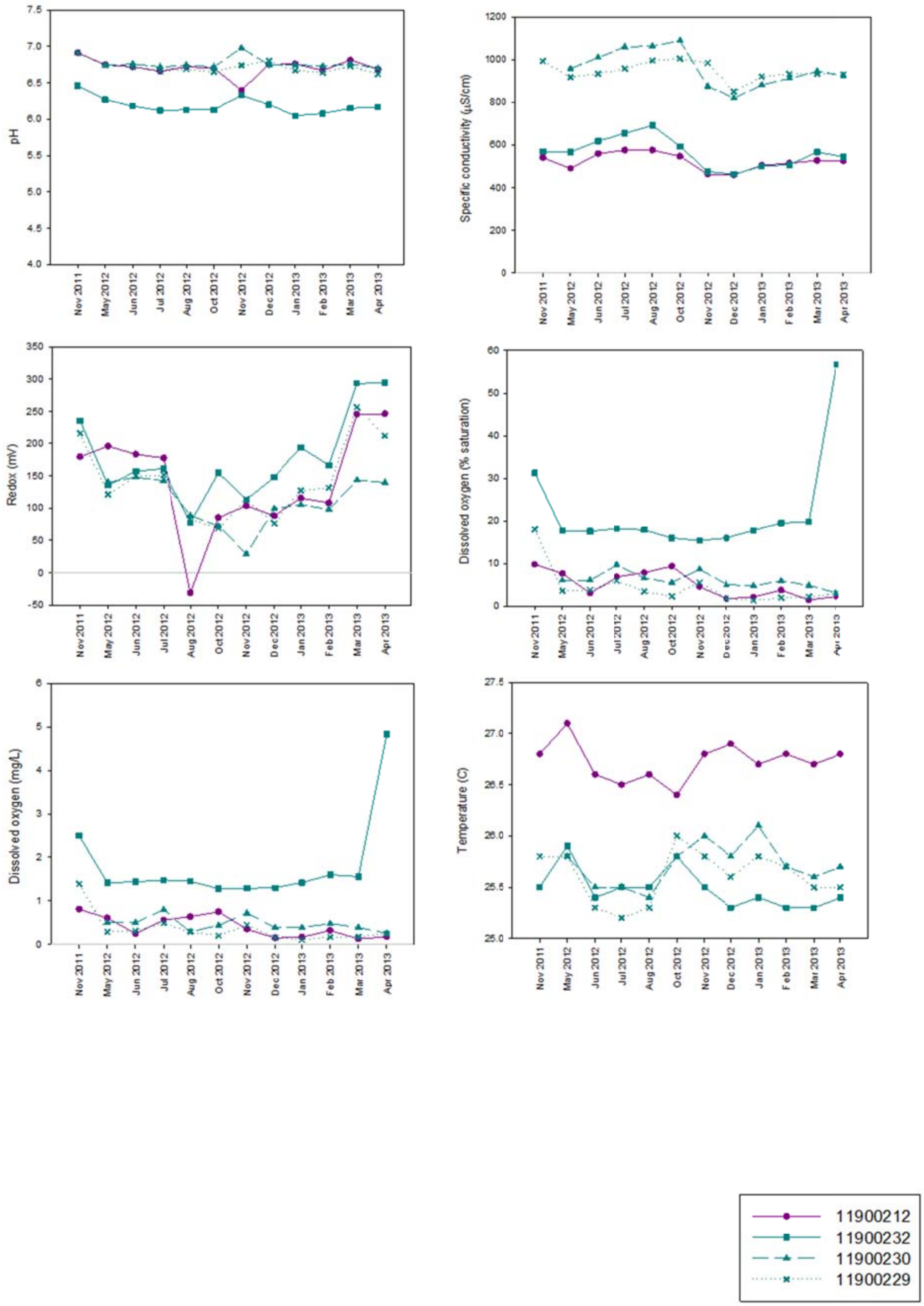
Appendix 1 – Pesticides analysed for and Limits of Reporting

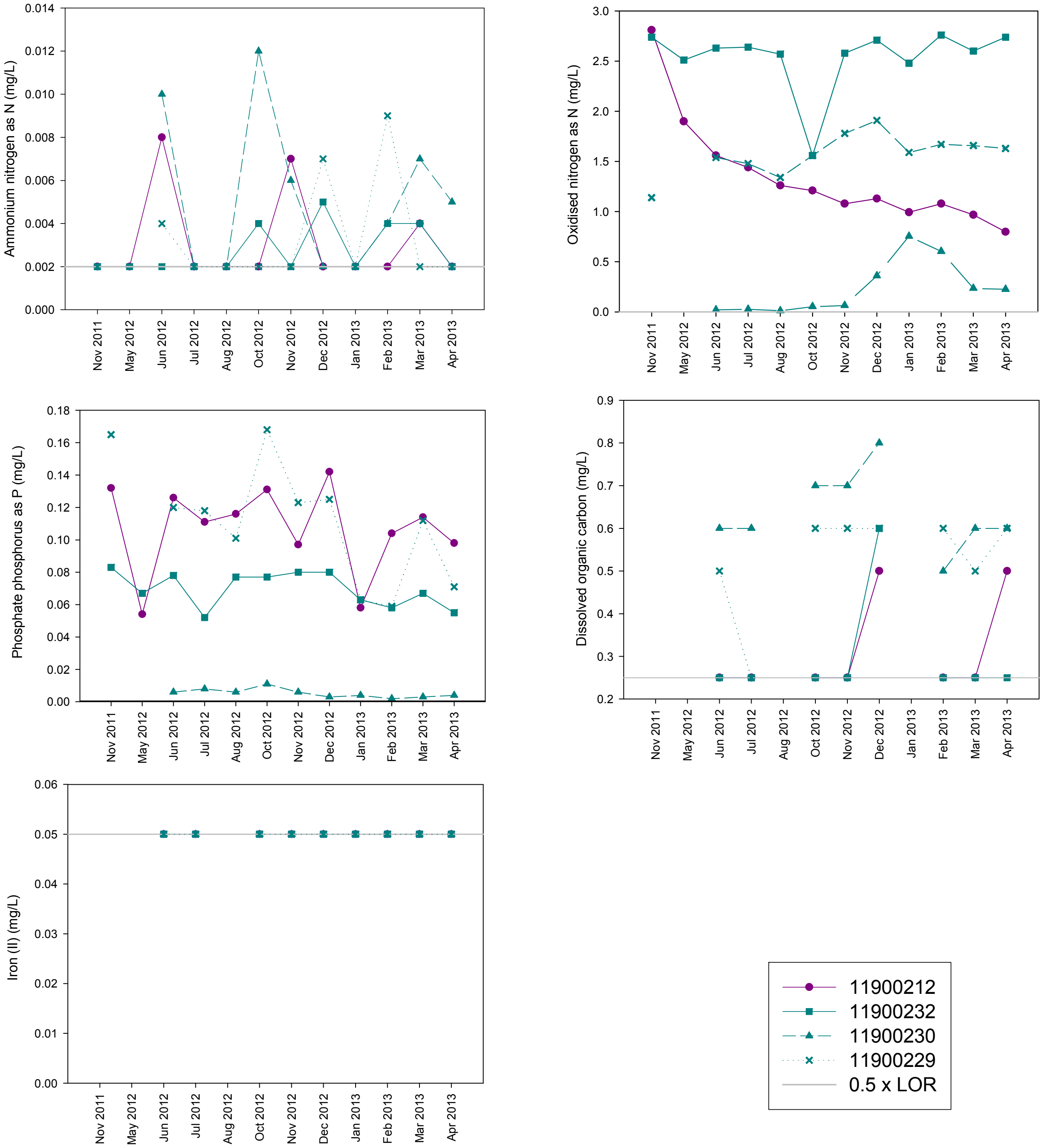
Pesticide	Limit of Reporting November 2011 and May 2012 (µg/L)	Limit of Reporting June 2012 - and April 2013 (µg/L)
Ametryn	0.005	0.001
Atrazine	0.005	0.001
Bromacil	0.005	0.001
Desethylatrazine	0.005	0.001
Desisopropylatrazine	0.005	0.001
Diuron	0.005	0.001
Fluometuron	0.005	0.001
Hexazinone	0.005	0.001
Imidacloprid	0.005	0.001
Metolachlor	0.005	0.001
Prometryn	0.005	0.001
Simazine	0.005	0.001
Tebuthiuron	0.005	0.001
Terbutryn	0.005	0.001
2,4-D	NT	0.004
2,4-DB	NT	0.004
Acifluorfen	NT	0.004
Clomazone	NT	0.001
Cyanazine	NT	0.001
Ethametsulfuron-methyl	NT	0.001
Fluroxypyr	NT	0.01
Flusilazole	NT	0.001
Haloxyfop (acid)	NT	0.004
Imazethapyr	NT	0.001
Isoxaflutole	NT	0.004
MCPA	NT	0.004
MCPB	NT	0.004
Mecoprop	NT	0.004
Mesosulfuron-methyl	NT	0.001
Metsulfuron-methyl	NT	0.001
Napropamide	NT	0.001
Propachlor	NT	0.001

Pesticide	Limit of Reporting November 2011 and May 2012 (µg/L)	Limit of Reporting June 2012 - and April 2013 (µg/L)
Propazin-2-hydroxy	NT	0.001
Sethoxydim (including Clethodim)	NT	0.008
Sulfosulfuron	NT	0.001
Terbuthylazine	NT	0.001
Terbuthylazine desethyl	NT	0.001
Total Imazapic	NT	0.05
Triclopyr	NT	0.004
Trifloxysulfuron	NT	0.004

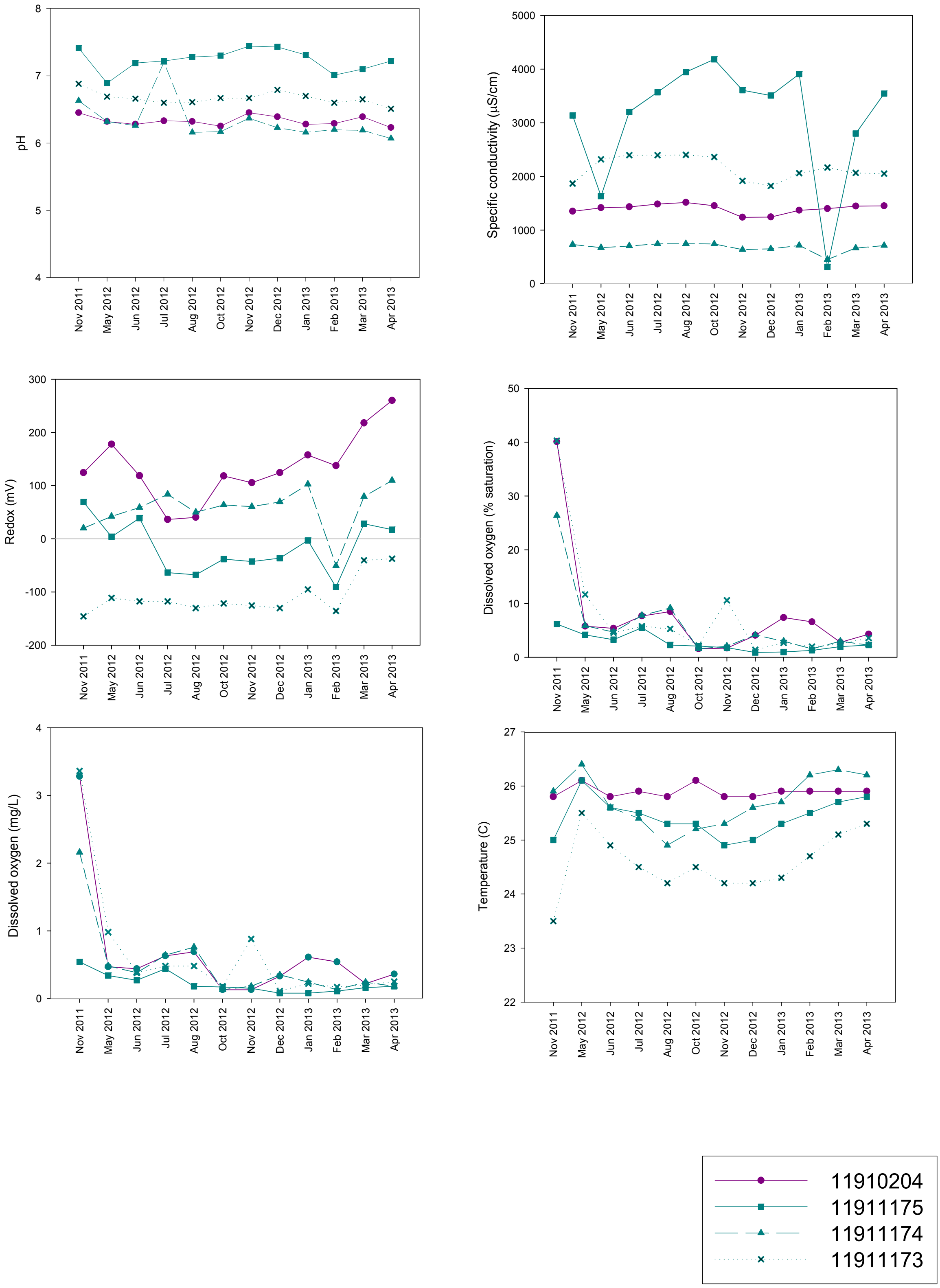
Note: NT means not tested for. These pesticides were added to the program after the May 2012 sampling round.

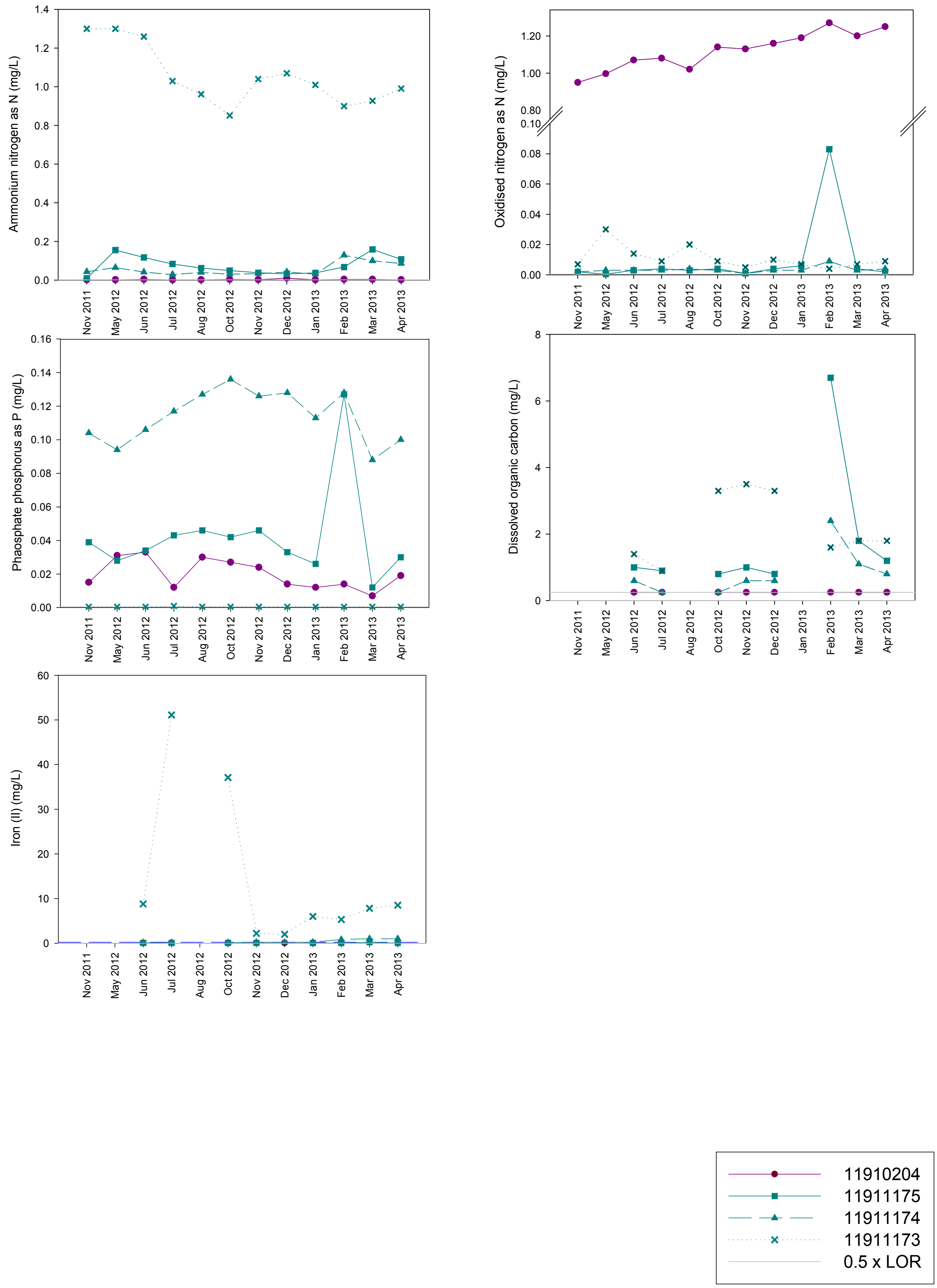
Appendix 2 – Physical and chemical measurements and nutrients detected in groundwater bores in the vicinity of Haughton River at Powerline


pH
Specific conductivity (µS/cm)
Redox (mV)
Dissolved oxygen (% saturation)
Dissolved oxygen (mg/L)
Temperature (C)
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013
11900212
11900232
11900230
11900229

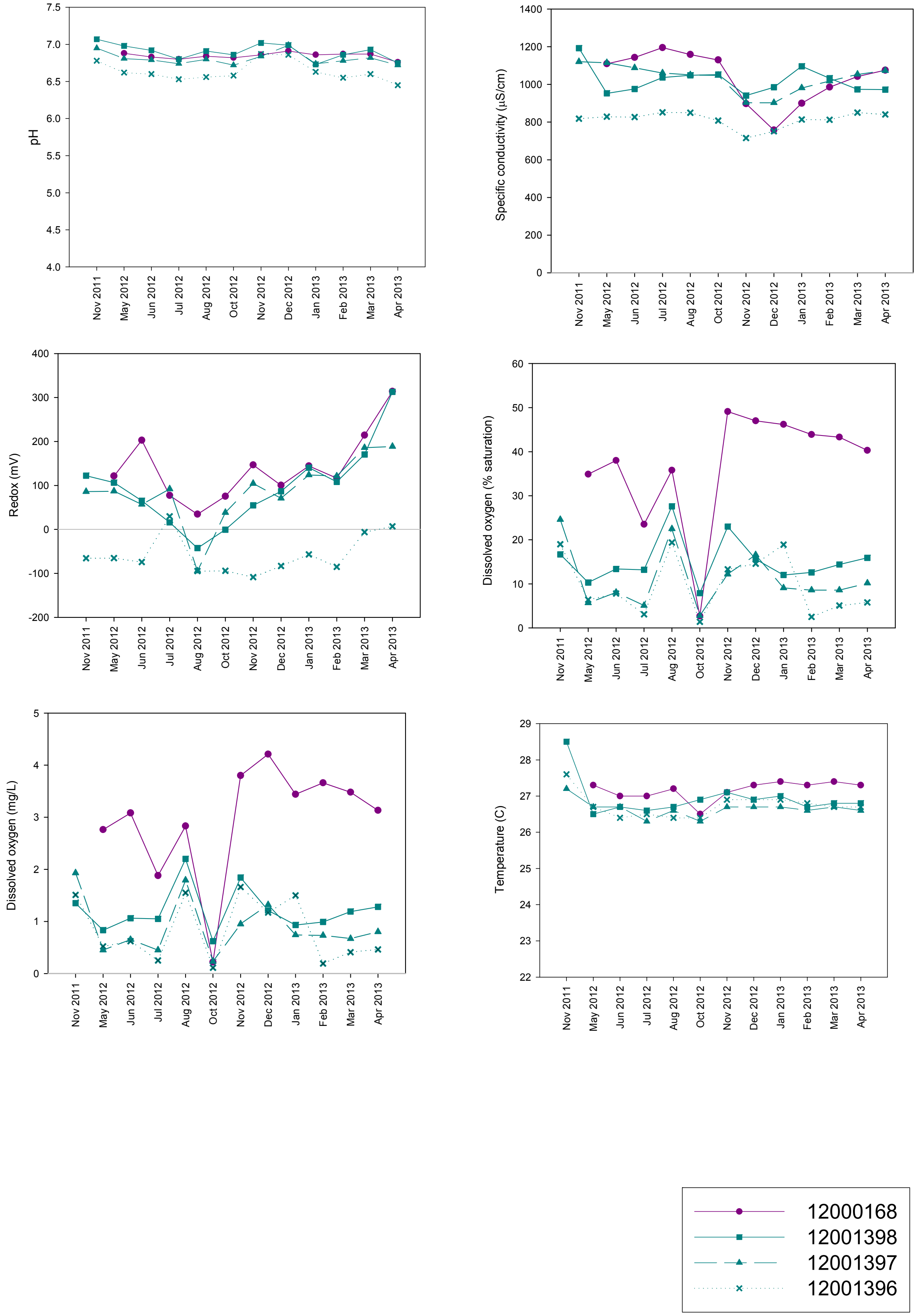

Ammonium nitrogen as N (mg/L)
Oxidised nitrogen as N (mg/L)
Phosphate phosphorus as P (mg/L)
Dissolved organic carbon (mg/L)
Iron (II) (mg/L)
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013
11900212
11900232
11900230
11900229
0.5 x LOR

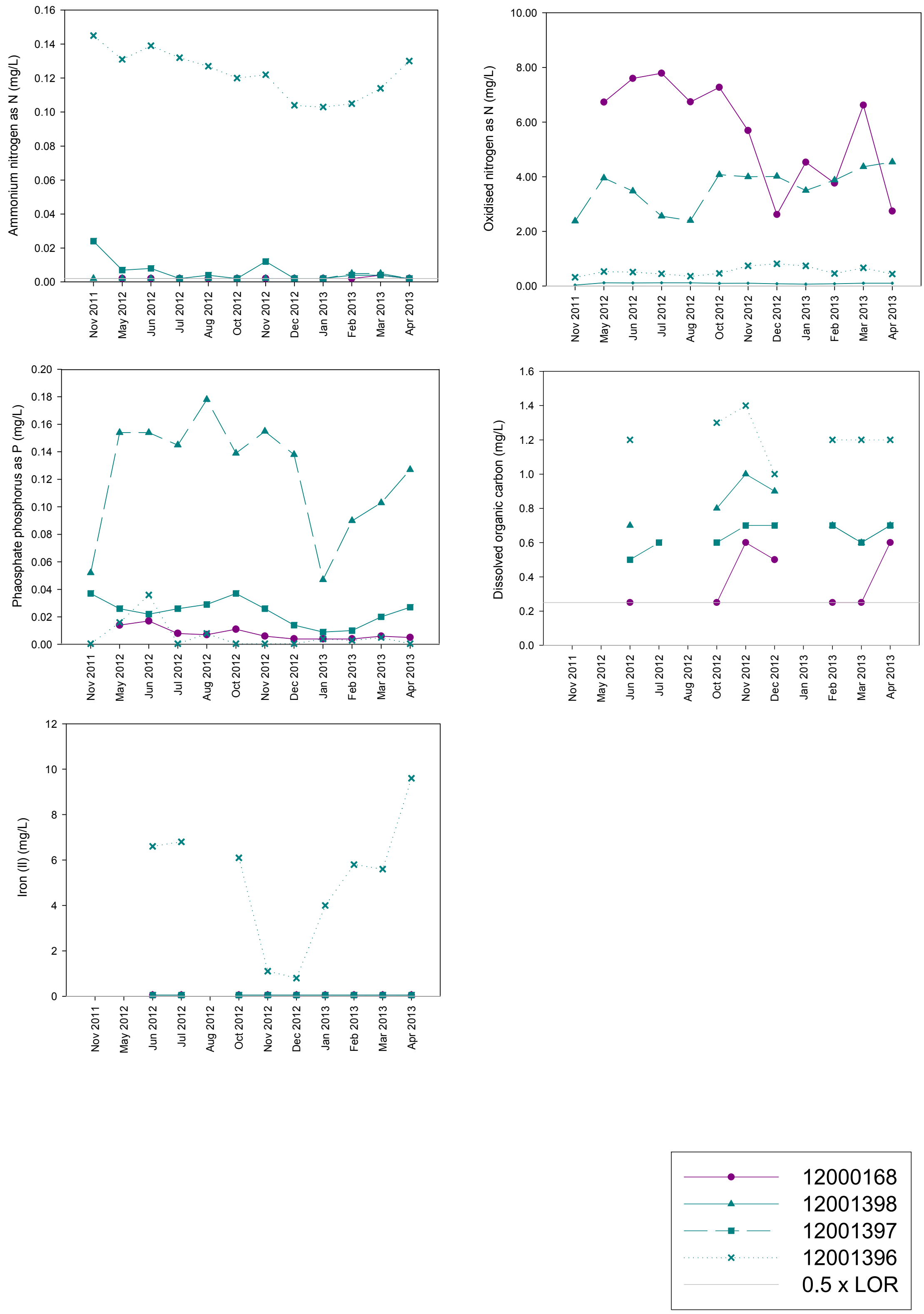
Appendix 3 – Physical and chemical measurements and nutrients detected in groundwater bores in the vicinity of Barratta Creek at Northcote


pH
Specific conductivity (µS/cm)
Redox (mV)
Dissolved oxygen (% saturation)
Dissolved oxygen (mg/L)
Temperature (C)
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013
11910204
11911175
11911174
11911173

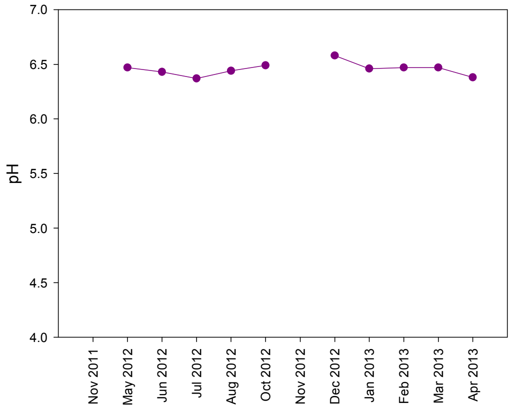

Ammonium nitrogen as N (mg/L)
Oxidised nitrogen as N (mg/L)
Phaosphate phosphorus as P (mg/L)
Dissolved organic carbon (mg/L)
Iron (II) (mg/L)
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013
11910204
11911175
11911174
11911173
0.5 x LOR

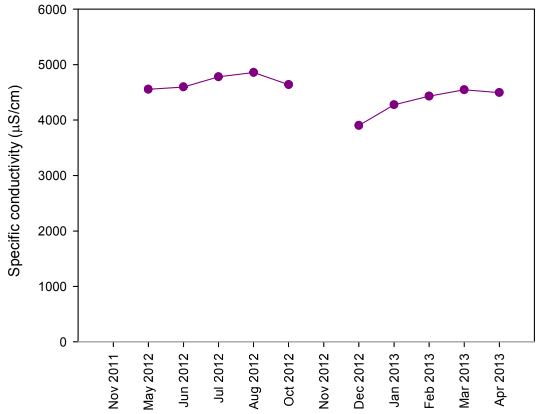
Appendix 4 – Physical and chemical measurements and nutrients detected in groundwater bores in the vicinity of Burdekin River at Clare

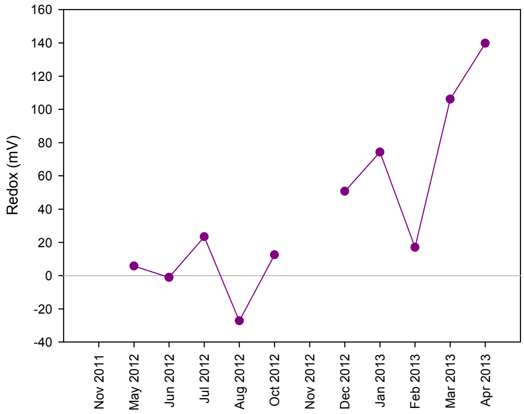

pH
Specific conductivity (µS/cm)
Redox (mV)
Dissolved oxygen (% saturation)
Dissolved oxygen (mg/L)
Temperature (C)
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013
12000168
12001398
12001397
12001396

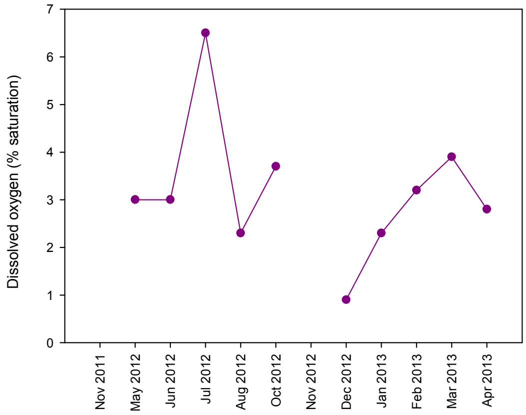

Ammonium nitrogen as N (mg/L)
Oxidised nitrogen as N (mg/L)
Phaosphate phosphorus as P (mg/L)
Dissolved organic carbon (mg/L)
Iron (II) (mg/L)
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013
12000168
12001398
12001397
12001396
0.5 x LOR

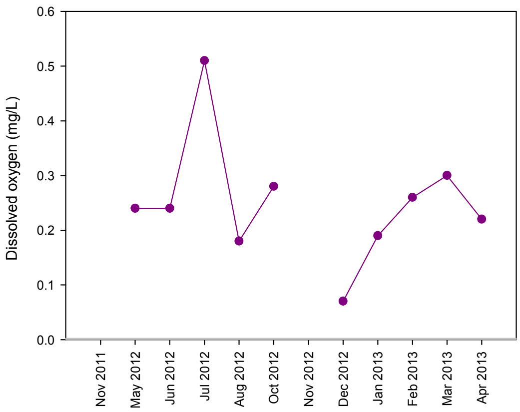
Appendix 5 – Physical and chemical measurements and nutrients detected in groundwater bores in the vicinity of Barratta Creek at Jerona

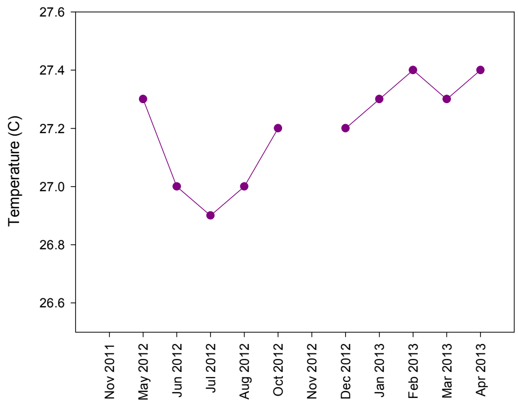

pH
7.0
6.5
6.0
5.5
5.0
4.5
4.0
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013

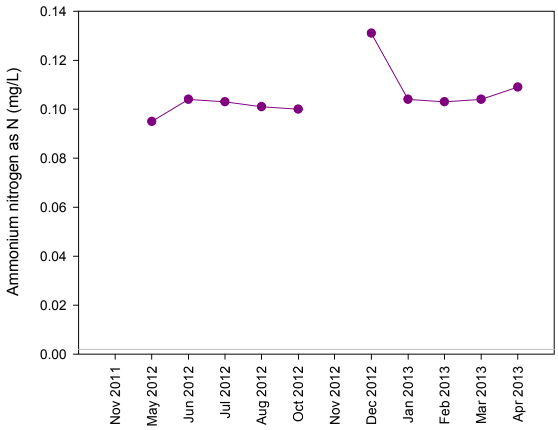

Specific conductivity (µS/cm)
6000
5000
4000
3000
2000
1000
0
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013

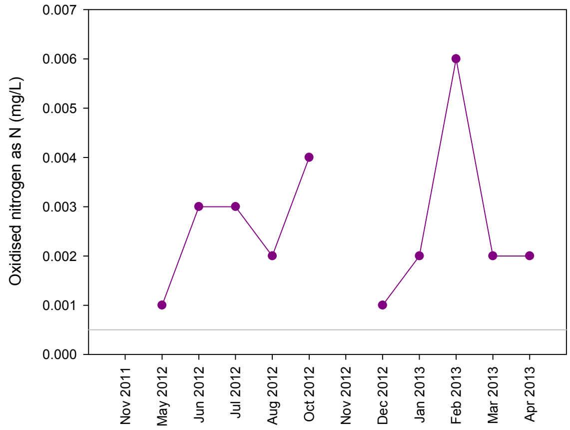

Redox (mV)
160
140
120
100
80
60
40
20
0
-20
-40
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013

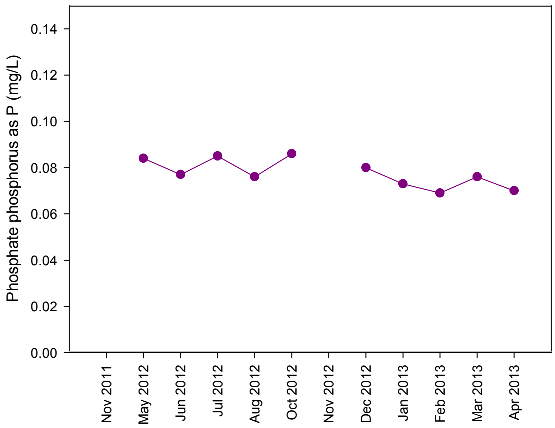

Dissolved oxygen (% saturation)
7
6
5
4
3
2
1
0
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013

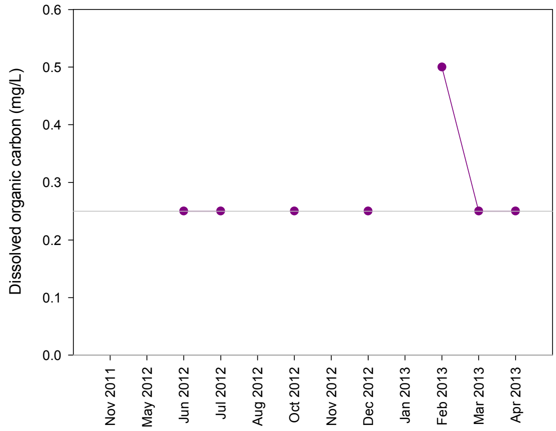

Dissolved oxygen (mg/L)
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013

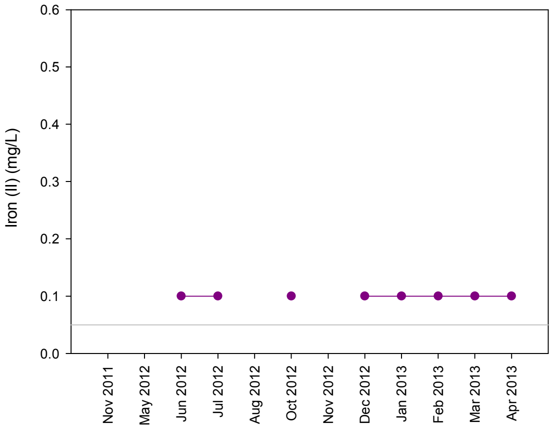

Temperature (C)
27.6
27.4
27.2
27.0
26.8
26.6
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013

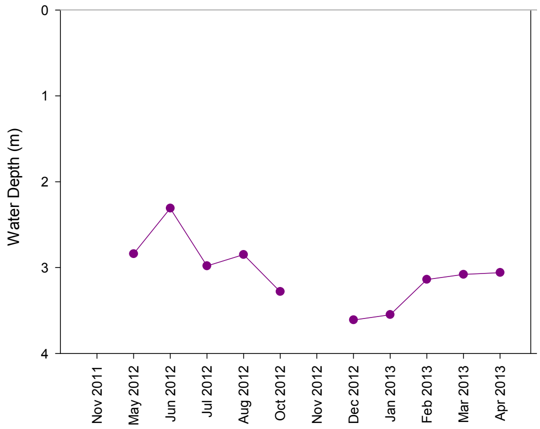

Ammonium nitrogen as N (mg/L)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013

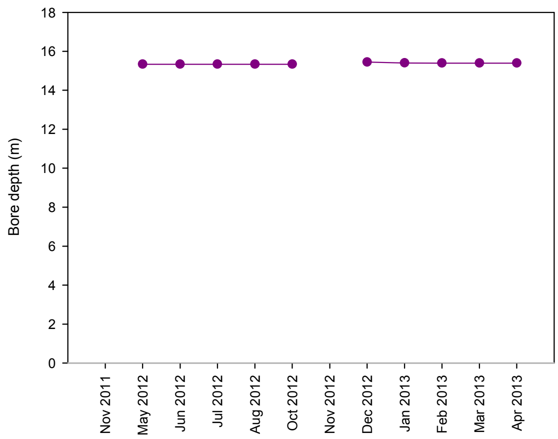

Oxidised nitrogen as N (mg/L)
0.000
0.001
0.002
0.003
0.004
0.005
0.006
0.007
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013


Phosphate phosphorus as P (mg/L)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013

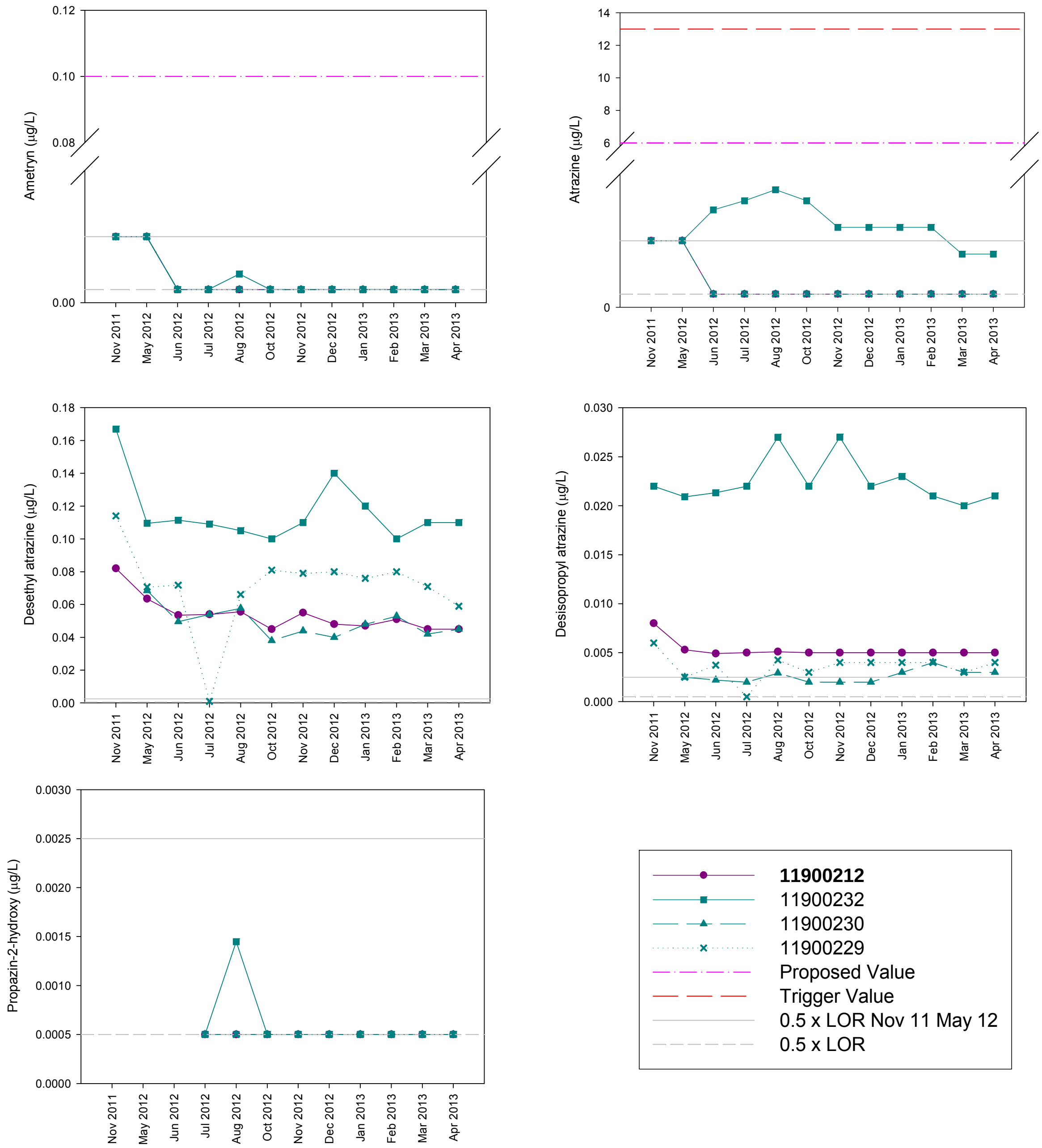

Dissolved organic carbon (mg/L)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013


Iron (II) (mg/L)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013

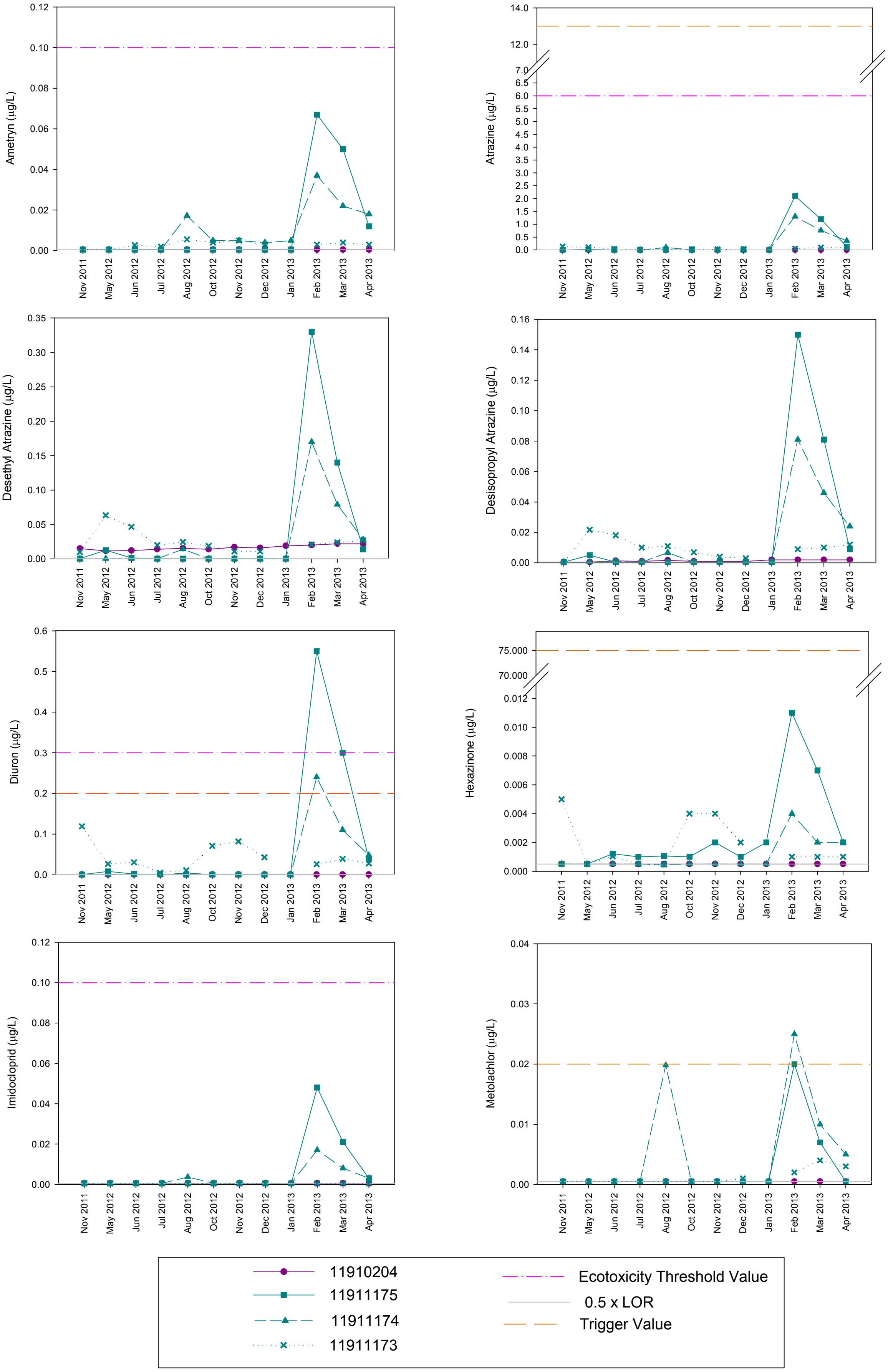

Water Depth (m)
0
1
2
3
4
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013

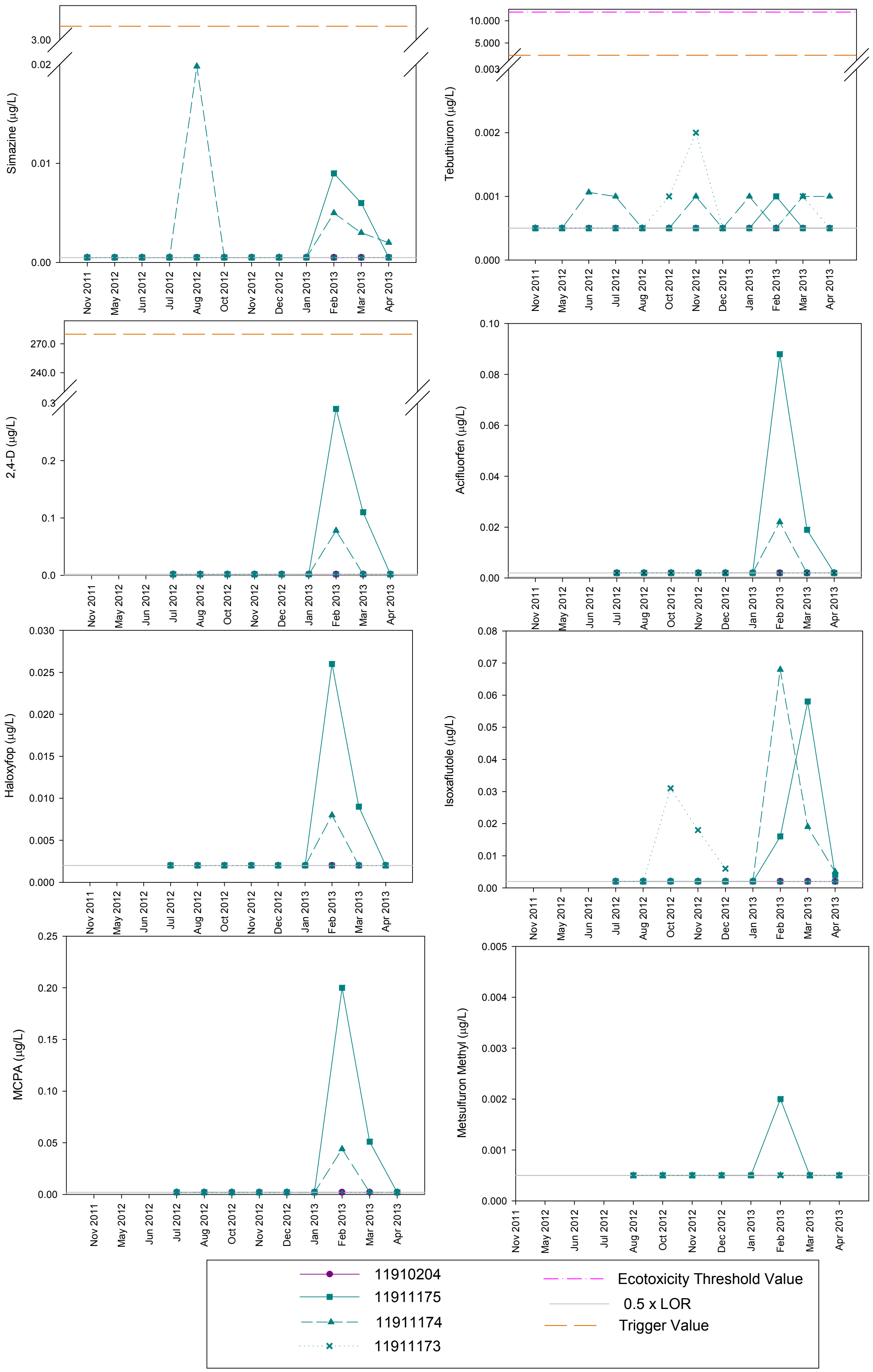

Bore depth (m)
0
2
4
6
8
10
12
14
16
18
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013

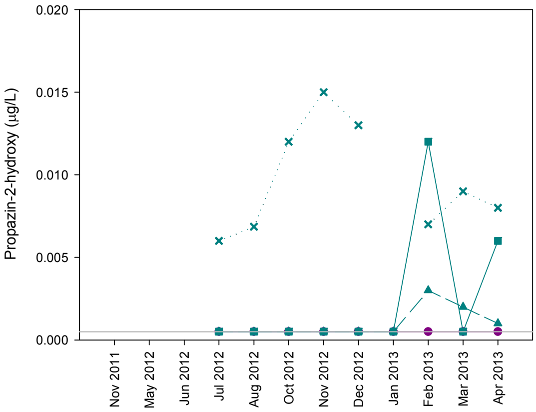
Appendix 6 – Pesticides detected in groundwater bores in the vicinity of Haughton River at Powerline

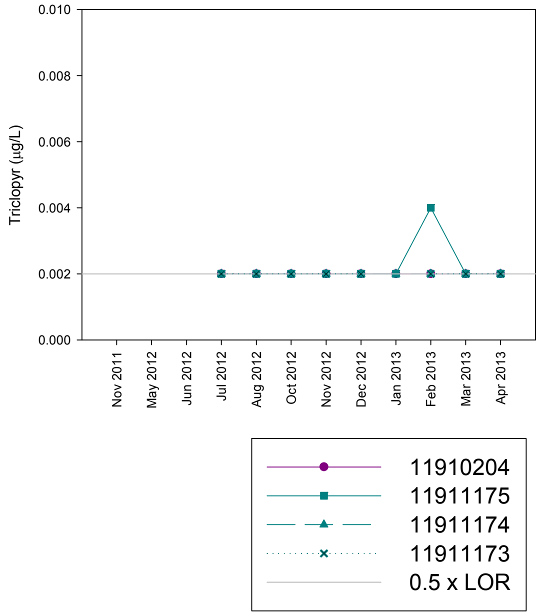

Ametryn (µg/L)
Atrazine (µg/L)
Desethyl atrazine (µg/L)
Desisopropyl atrazine (µg/L)
Propazin-2-hydroxy (µg/L)
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013
11900212
11900232
11900230
11900229
Proposed Value
Trigger Value
0.5 x LOR Nov 11 May 12
0.5 x LOR

Appendix 7 – Pesticides detected in groundwater bores in the vicinity of Barratta Creek at Northcote

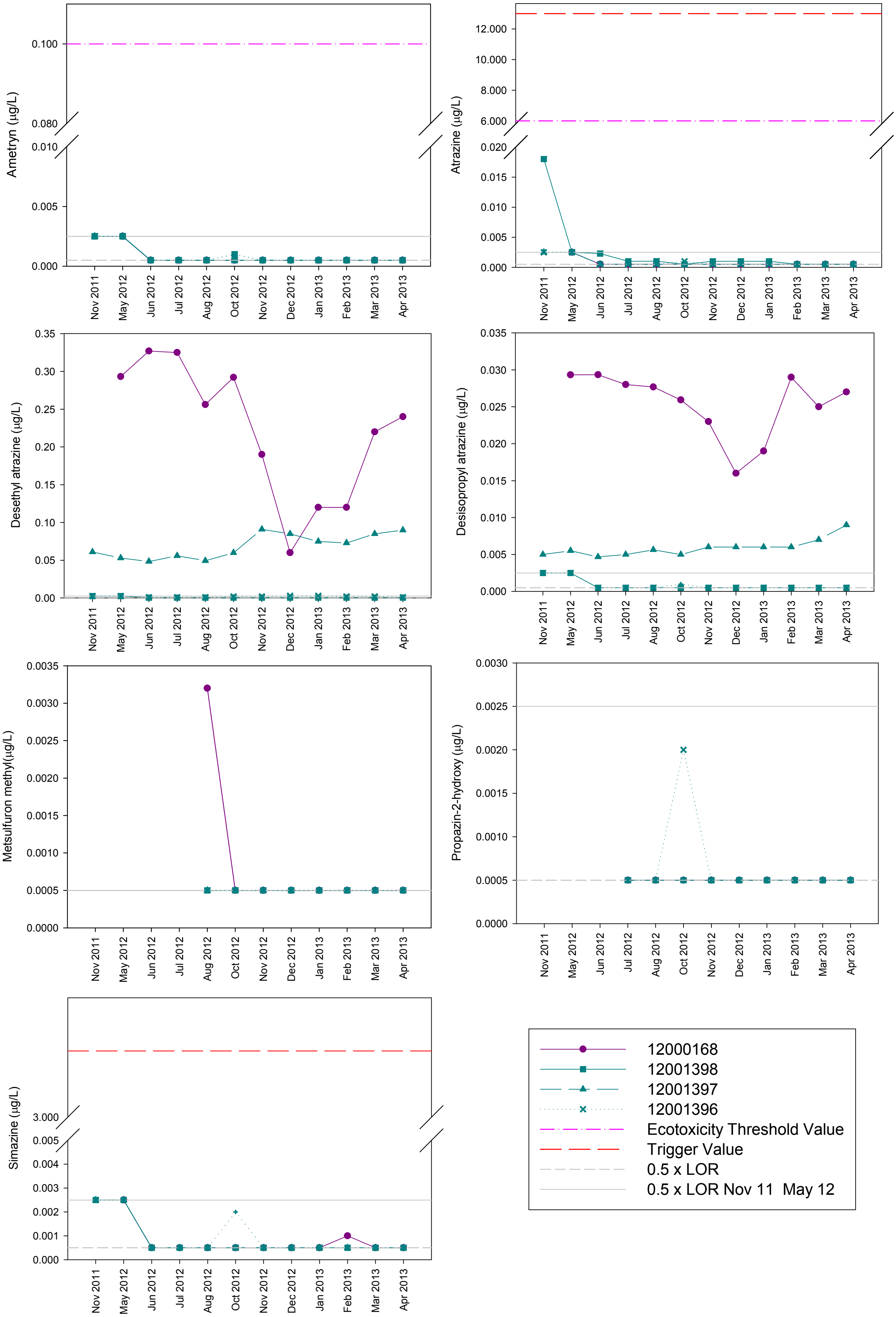

Ametryn (µg/L)
Atrazine (µg/L)
Desethyl Atrazine (µg/L)
Desisopropyl Atrazine (µg/L)
Diuron (µg/L)
Hexazinone (µg/L)
Imidocloprid (µg/L)
Metolachlor (µg/L)
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013
11910204
11911175
11911174
11911173
Ecotoxicity Threshold Value
0.5 x LOR
Trigger Value


Simazine (µg/L)
Tebuthiuron (µg/L)
2,4-D (µg/L)
Acifluorfen (µg/L)
Haloxyfop (µg/L)
Isoxaflutole (µg/L)
MCPA (µg/L)
Metsulfuron Methyl (µg/L)
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013
11910204
11911175
11911174
11911173
Ecotoxicity Threshold Value
0.5 x LOR
Trigger Value

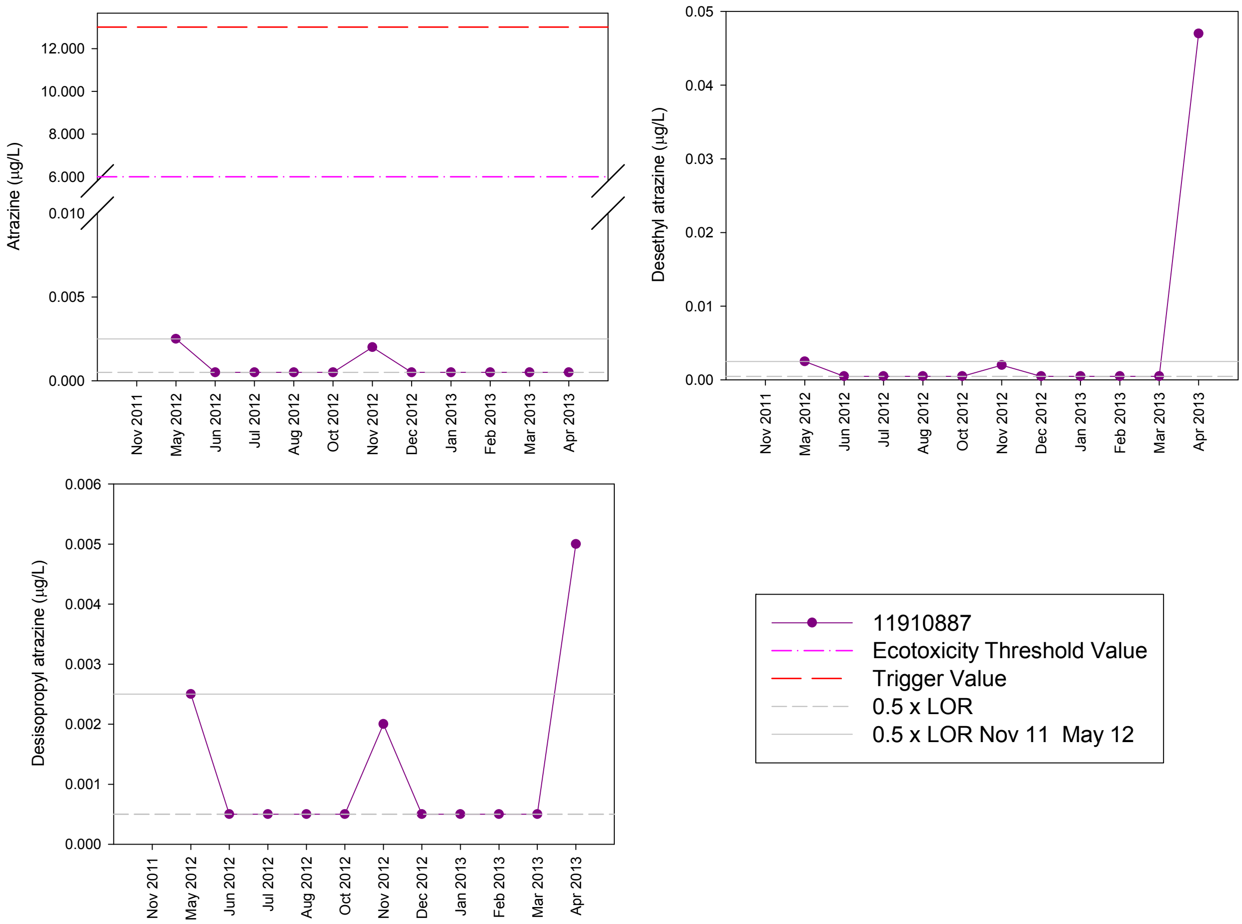

Propazin-2-hydroxy (µg/L)
0.020
0.015
0.010
0.005
0.000
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013


Triclopyr (µg/L)
0.010
0.008
0.006
0.004
0.002
0.000
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013
11910204
11911175
11911174
11911173
0.5 x LOR

Appendix 8 – Pesticides detected in groundwater bores in the vicinity of the Burdekin River at Clare


Ametryn (µg/L)
Atrazine (µg/L)
Desethyl atrazine (µg/L)
Desisopropyl atrazine (µg/L)
Metsulfuron methyl(µg/L)
Propazin-2-hydroxy (µg/L)
Simazine (µg/L)
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013
12000168
12001398
12001397
12001396
Ecotoxicity Threshold Value
Trigger Value
0.5 x LOR
0.5 x LOR Nov 11 May 12

Appendix 9 – Pesticides detected in groundwater bores in the vicinity of the Barratta Creek at Jerona


Atrazine (µg/L)
Desethyl atrazine (µg/L)
Desisopropyl atrazine (µg/L)
Nov 2011
May 2012
Jun 2012
Jul 2012
Aug 2012
Oct 2012
Nov 2012
Dec 2012
Jan 2013
Feb 2013
Mar 2013
Apr 2013
11910887
Ecotoxicity Threshold Value
Trigger Value
0.5 x LOR
0.5 x LOR Nov 11 May 12