

## Herbicides, pesticides and nutrients in the Tindall aquifer, Katherine Region



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*Cover Photograph: Water sampling at Katherine Hot Springs, 2015. Photo by Liza Schenkel.*

## Acknowledgments

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## 1. Summary

This study was the first in a planned series of surveys of groundwater quality for water allocation plan areas of the Top End.

In particular, this study aimed to:

1. investigate whether any pesticide and/or herbicide residues are currently present in groundwater of the Tindall aquifer
2. investigate whether nutrient concentrations, in particular NO<sub>3</sub> (nitrate), in the Tindall aquifer are currently elevated and whether elevated concentrations are widespread
3. provide a baseline for future studies of groundwater quality in the region

The survey examined 24 bores and 3 springs in the Katherine region of the Tindall aquifer. The bores were selected to be spread across the aquifer and included both private equipped bores used for domestic or irrigation purposes and NT Government monitoring bores. The sites included bores in agricultural, rural, urban and undeveloped areas.

The ionic composition of waters from the 27 sites was very similar across the study area confirming that they are of the same water type and hydrogeological source.

Total and soluble nutrient concentrations, with the exception of nitrate, were low at all sites. Nitrate concentrations were variable across the aquifer ranging from <0.001 to 1.85 mg\_N/L.

Pesticides or herbicides were detected at 13 of the 27 sites. Seven different pesticides and herbicides and/or their breakdown products were found, with no more than three different herbicides or pesticides found at any one site.

The herbicide atrazine and its breakdown products desethyl atrazine and desisopropyl atrazine were the most widespread contaminants and were present at 37% (10) of sites. The other detected chemicals were the herbicides tebuthiuron, simazine, haloxyfop and imazapyr, the insecticide imidacloprid and 2,4-di-t-butylphenol, a UV stabiliser.

There was no significant relationship of land use or depth of the bore screen with either nutrient or pesticide detections, although the highest nitrate concentrations were found under intensive agricultural land use. .

Both nitrate and pesticide concentrations were low compared to many other regions of Australia and did not exceed guidelines for drinking water or environmental protection. A comparison with dry season river water concentrations of the detected chemicals suggests the groundwater contamination is diluted by both uncontaminated groundwater and Cretaceous sandstone groundwater-fed river flow.

The detection of any aquifer contamination should serve as a reminder to apply best practice in the storage, application and disposal of these chemicals.

## 2. Introduction

### 2.1. Background and study aims

In 2011, traces of pesticides and herbicides were detected in dry season flows monitoring of the Katherine River (Schult 2012). During the dry season, flows in the Katherine River are supplied mainly by groundwater from the Tindall limestone aquifer, suggesting that groundwater in the region might also be the source of the contamination. Furthermore, groundwater inputs from the Tindall aquifer to the Katherine River are known to contain relatively high concentrations of nitrate, a common anthropogenic contaminant of groundwater, in comparison to inputs from other aquifers in the region (e.g. Lawrie 2014, Schult 2014A).

In response to these findings, the Department of Land Resource Management commenced a series of baseline studies of selected aquifers of the Top End to examine groundwater quality. This study is the first in the planned series.

In particular, this study aimed to:

4. investigate whether any pesticide and/or herbicide residues are currently present in groundwater of the Tindall aquifer
5. investigate whether nutrient concentrations, in particular NO<sub>3</sub> (nitrate), in the Tindall aquifer are currently elevated and whether elevated concentrations are widespread
6. provide a baseline for future studies of groundwater quality in the region

### 2.2. The Tindall Limestone Aquifer

The Tindall aquifer is part of the Daly Basin, a geological formation that was created 400 to 500 million years ago, when a shallow sea extended over the northern and central parts of the Northern Territory (Tickell 2009). The Daly Basin extends from the lower to middle reaches of the Daly River in the north-west to the central part of the Top End south of Katherine (Figure 1A).

The basin consists of three main layers that formed at different times and during different climatic conditions: the Tindall Limestone, the Jinduckin Formation and the Ooloo Dolostone (Figure 1 B,C). The Tindall Limestone and Ooloo Dolostone are primarily calcium/magnesium carbonate rocks of marine origin while the Jinduckin Formation was sourced from a mixture of land-derived and calcium/magnesium carbonate sediments from the intertidal zone that formed when sea levels were lower. Mild tectonic forces caused the limestone crust to sag, so that the same type of rock that is found near the surface at the edge of the basin is found at depths of up to 700 m near its centre (Figure 1C).

Carbonate rock such as that found in the Tindall and Ooloo formations, dissolves in water over geological timeframes, becomes porous and forms caverns and fractures. The porous rock acts like a sponge and holds large amounts of water.

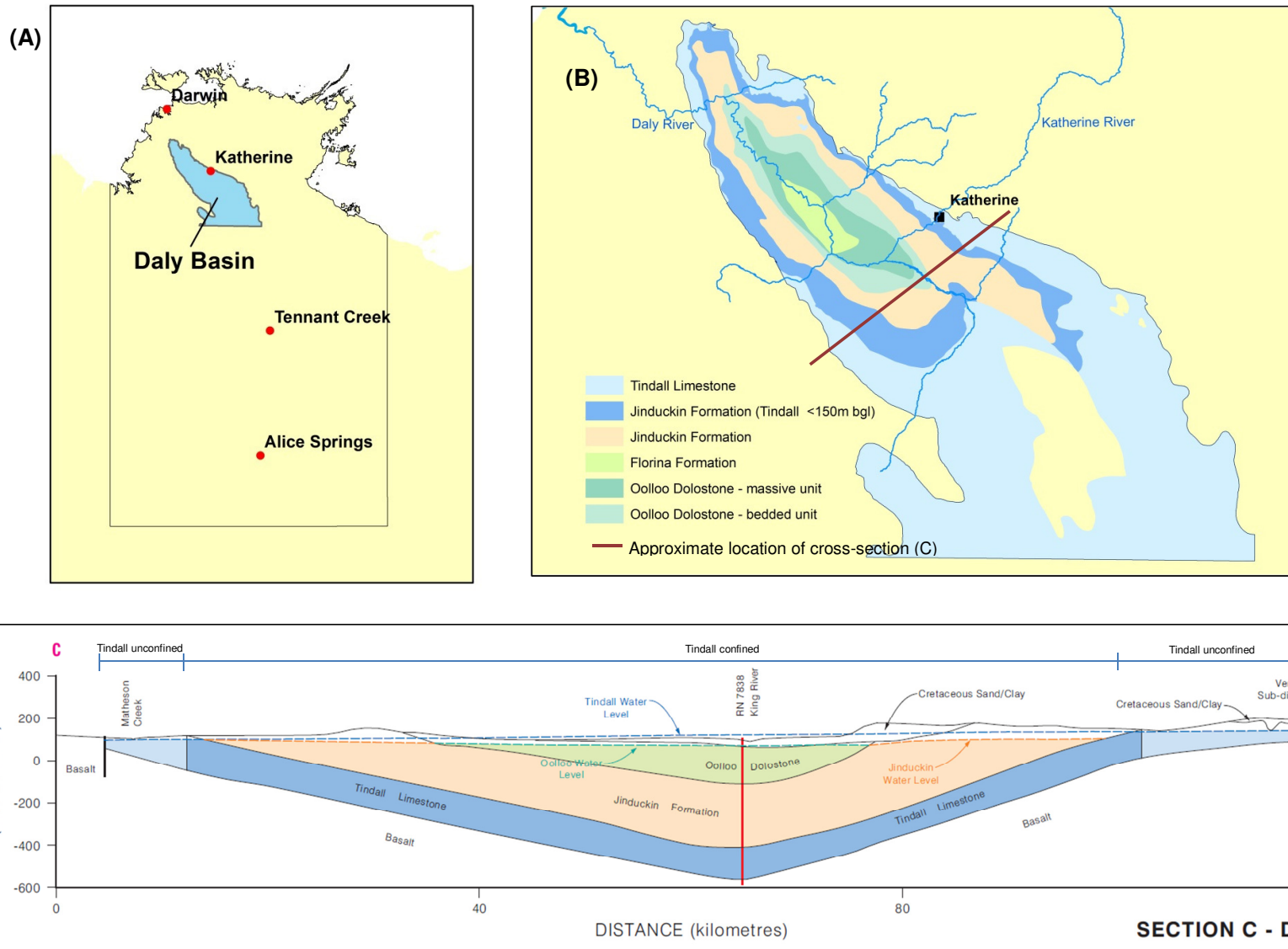
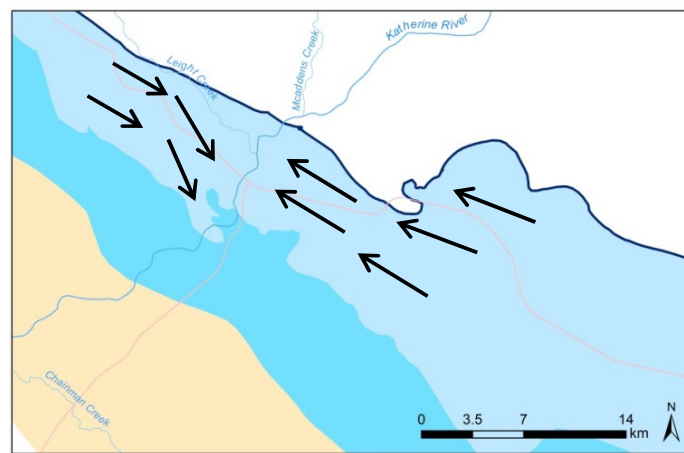


Figure 1. The Daly Basin. Location (A), Aquifers (B) and cross-section (C). (Image (C) from Tickell 2007)

Water from the aquifer moves through the rock, driven by gravity, and is discharged through springs and seepages at low points in the landscape, while recharge occurs from the surface when rainwater moves through the top soil into the rocks below.

Where the aquifer is confined by impervious layers of rock above it, recharge cannot occur from the top. However, the confined areas of the aquifer can be recharged through lateral movement of water from unconfined areas. The Tindall aquifer has unconfined (recharge and discharge) areas along the edge of the Daly Basin, while it is confined by the Jinduckin and Ooloo formations towards the centre (Figure 1C). The Jinduckin Formation overlies the western extent of the Tindall Aquifer within the study area and consists predominately of shale and siltstone with little fractured porosity. This represents a barrier to vertical infiltration of water and potential contaminants from the surface.

The flow of groundwater usually takes the most direct path from recharge zones to low lying discharge zones. In the Katherine region, this means the main flow of groundwater in the unconfined section is parallel to the edges of the Tindall aquifer towards the Katherine River while there is little flow from the edges towards the centre (Tickell 2009, Figure 2).



**Figure 2. Approximate direction of main groundwater flow in the Katherine region Tindall aquifer.**

### **2.3. Use of groundwater**

The perennial streams of the Top End are dependent on groundwater to maintain flows during the dry season. The Tindall aquifer provides the majority of dry season flow in the Katherine River and the lower Edith and Fergusson Rivers through springs and seepages within the river beds, with a lesser amount of water being contributed by an overlying Cretaceous aged aquifer in the upper parts of the catchment. These flows are essential to maintain the character and values of the Katherine/Daly River ecosystem, including its diverse aquatic flora and fauna, its recreational values and its importance for tourism.

The aquifer is also the main source of water for urban and agricultural development in the Katherine region where groundwater is used extensively for the irrigation of crops and

gardens and watering of livestock, and also provides part of the drinking water supply for the town of Katherine. The Katherine Tindall Water Allocation Plan (Connor 2009) regulates the use of the resource to ensure that a balance is maintained between environmental and human demands for groundwater.

#### **2.4. Risks to groundwater quality**

Groundwater quality is naturally influenced by the geology of the aquifer it is stored in. The type of rock the water is stored in is reflected in the minerals that are dissolved in the water.

Changes to groundwater quality can occur when chemicals at the surface reach the water table by leaching through the soil or more directly through contamination of bores and sinkholes. Because it takes time for these substances to move through the soil and the aquifer, shallow, unconfined areas are most at risk from surface contamination since there is no physical barrier of impervious rock. Processes that generate a change in groundwater quality can be natural or caused by human activities.

The most common anthropogenic (human-generated) contaminant of groundwater is nitrate. Nitrate occurs naturally and is produced from the decomposition of organic material and the fixation of atmospheric nitrogen by bacteria and its subsequent oxidation. These processes occur in soils and plants. The main anthropogenic sources of nitrate are sewerage discharge, animal waste and the agricultural application of industrial fertilisers which usually contain nitrogen in the form of ammonia or nitrate, as well as atmospheric deposition of nitrogen from burning fossil fuels.

While other nutrients, such as phosphorus or organically bound nitrogen adsorb to soil particles and are therefore filtered out as water passes through the soil, nitrate is easily dissolved in water and can be carried deep into the aquifer.

The removal of nitrate from soils only occurs if nitrate is taken up by plants for further growth, or through the process of denitrification, the biological reduction of nitrate to molecular  $N_2$  (a gas, which is released back into the atmosphere). This can only occur under certain anaerobic soil conditions, however, these conditions are not common in the unsaturated zone above the water table, so that once nitrate moves below the root zone of plants, it is likely to persist and reach the aquifer below.

Nitrate contamination of groundwater can potentially lead to the eutrophication of aquatic ecosystems and cause algal blooms and other changes to the aquatic flora, when contaminated groundwater is discharged to rivers and streams.

Other human-made chemicals, including pesticides and herbicides, can also enter aquifers and contaminate groundwater. Pesticides and herbicides are used widely in the community with uses ranging from small scale applications around the home and garden, termite control around buildings, larger scale herbicide spraying around infrastructure and roads to the control of noxious weeds on rural blocks and applications of pesticides to crops and livestock by farmers and the agricultural industry.

Where these chemicals are stored or applied incorrectly, they can enter the groundwater, for example via backflow through faulty valves of fertigation systems or when excessive amounts of chemicals or fertilisers are applied to crops and leach through the soil into the aquifer below. Chemicals that are highly water-soluble pose a higher risk to groundwater

because they are easily carried from the soil surface into the aquifer by rain or irrigation. In Australia, the Australian Pesticides and Veterinary Medicines Authority (APVMA) regulates the registration and use of pesticides.

## **2.5. Current knowledge of groundwater quality**

The Department of Land Resource Management has been monitoring nutrient levels in the Katherine River as well as in springs and selected monitoring bores biannually since 2012. Prior to that, there has been project-specific surface water monitoring that included nutrients in the Katherine River. The data show that groundwater inflows to the Katherine River from the Tindall aquifer have higher nitrate levels than waters that originate from the sandstone aquifer of the Arnhem Land plateau that supplies the upper reaches of the river. Nitrate concentrations in the Katherine River increase significantly where it intersects the Tindall aquifer and receives inflows from numerous springs and seepages in the Katherine region (e.g. Lawrie 2014, Schult 2014A).

Nutrients in groundwater are not routinely monitored by the Northern Territory Government, however, there is a requirement for nitrate to be measured for human health reasons whenever a bore is established. The detection limits that apply to these samples are generally much higher than those required to detect changes at environmental levels.

There are no published studies of pesticides and herbicides in groundwater in the Katherine region. Historically, the main focus of groundwater monitoring by the Department of Land Resource Management has been on water availability for consumptive use. Groundwater quality is also monitored but is mainly restricted to general water quality parameters and, more recently, heavy metals (e.g. Wagenaar 2013a,b, Lawrie 2014,).

However, some recent dry season surveys of pesticides and herbicides in streams and springs in the Top End have detected traces of herbicides and pesticides at very low concentrations in many groundwater-fed streams, including the Katherine River (Schult 2012, Schult 2014b, Schult 2016).

## **3. Methods**

### *Site selection*

The survey examined 24 bores and 3 springs in the Katherine region of the Tindall aquifer. Sites were selected to be spread across the aquifer and included both private bores equipped with pumps and used for domestic or irrigation purposes and NT Government monitoring bores. They included bores in agricultural, rural, urban and undeveloped areas.

The majority of sites were located in the unconfined section of the aquifer, where the limestone is not covered by an impermeable layer of rock. The risk of contamination is highest in this area, since there is no barrier to prevent seepage from the surface from entering the aquifer. Five of the bores were located in areas where the aquifer is confined by the overlying Jinduckin formation (**Figure 3**) to enhance spatial coverage.



All the bores, including those in the confined areas, pump water from the Tindall aquifer at different depths, depending on how close to the surface the limestone is located.

Each site was allocated one of four land use categories (agricultural, industrial/urban, rural/domestic or natural environment) according to the immediate surrounding area using Google Earth imagery.

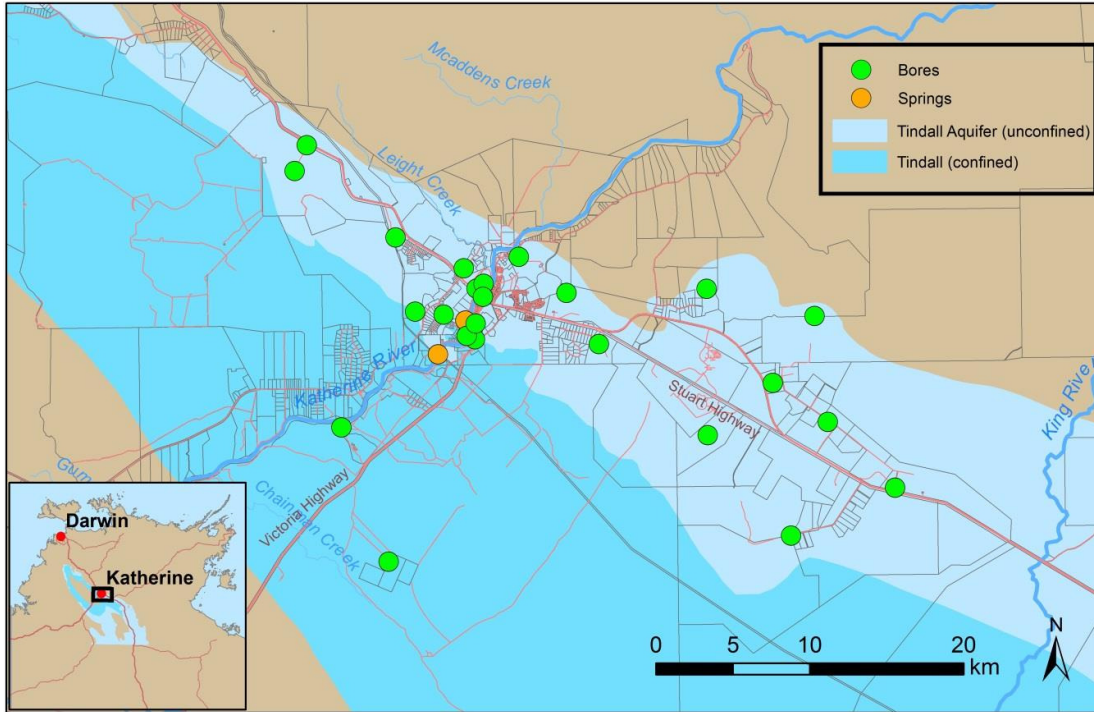


Figure 3. Location of sample sites in the Katherine Tindall aquifer region.

### Bore and spring sampling

Field measurements and water samples were collected from all springs and bores. In the springs field measurements were taken *in situ* and water samples collected using a sampling pole to submerge bottles into the flow.

Where bores were equipped with a pump and used for production, samples were collected from a tap as close to the bore head as possible. Unequipped bores were purged to remove stagnant water in the bore using a mobile pump and samples taken when field measurements of water quality were stable. Field measurements from bores were made using bore water collected in a bucket. .

Field measurements of temperature, pH, electrical conductivity (EC), dissolved oxygen (DO) and turbidity were measured with a Hydrolab Quanta multi-parameter probe (Ott Hydromet GmbH). Pesticide and herbicide samples were collected in three separate glass bottles for pesticide, herbicide and glyphosate analysis. Herbicide and glyphosate bottles were spiked with the preservative thiosulfate. All herbicide and pesticide samples were refrigerated in the

field and upon return to the laboratory. Samples were analysed by the Queensland Department of Health's Forensic and Scientific Services for a large range of pesticides and herbicides. A total of 180 substances were tested for, including organochlorine pesticides (e.g. DDT, Dieldrin), organophosphate pesticides (e.g. chlorpyrifos), synthetic pyrethroids, triazine herbicides, glyphosate ("Roundup") and other common herbicides. A full list of analytes is provided in Appendix A.

Nutrient samples were collected in polyethylene sample bottles for total and soluble nutrients. Soluble nutrient samples were filtered in the field through 0.45 µm glass-fibre filters. All nutrient samples were frozen in the field and analysed by the Northern Territory Environmental Laboratories (NTEL Intertek) for total nitrogen and total phosphorus, nitrite (NO<sub>2</sub>), nitrate (NO<sub>3</sub>), ammonia (NH<sub>3</sub>) and filterable phosphorus (FRP). Samples for general water quality parameters (alkalinity, hardness, pH, conductivity) and major cations (K<sup>+</sup>, Na<sup>2+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) and anions (Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-</sup>) were collected in polyethylene bottles and kept refrigerated until they were analysed by NTEL Intertek, Darwin. All samples were analysed according to APHA (2005) standard methods.

Additional samples were collected for ageing of water using C<sup>14</sup>, stable isotope and deuterium methods. Detailed methods and results of this work are reported separately (Tickell 2016).

#### *Historical data*

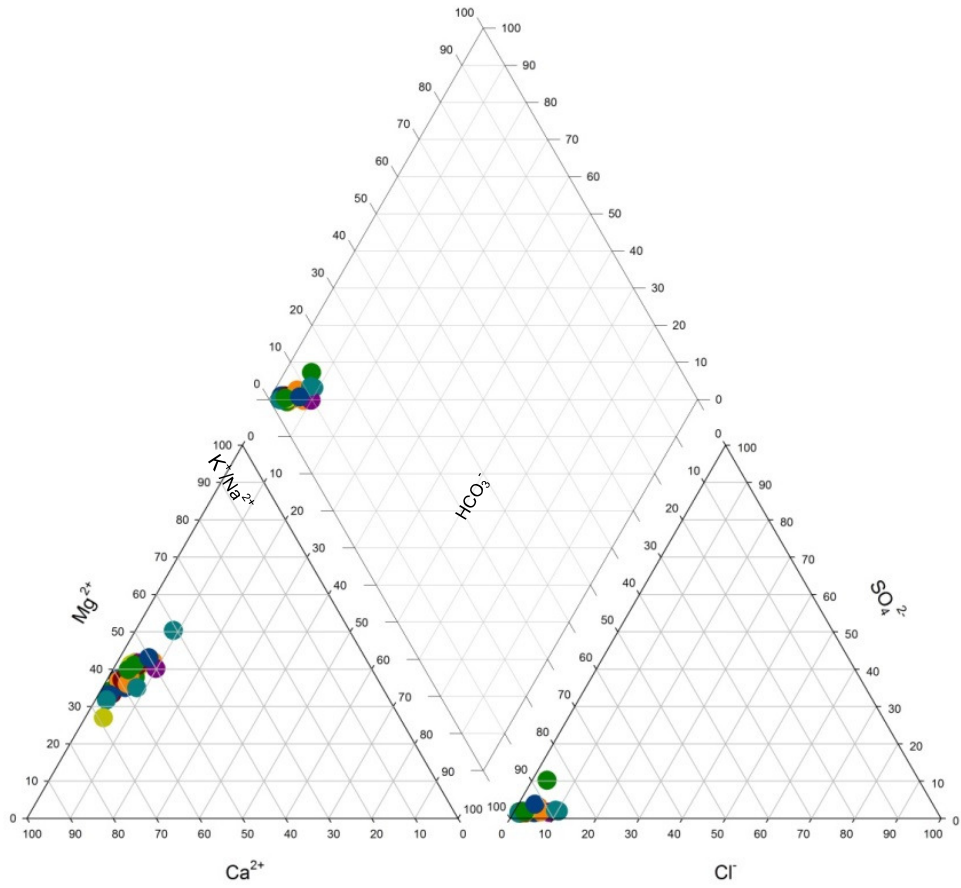
For comparison of historical nitrate concentrations with current results, data from the DLRM water quality database was used where available. Bore water quality is routinely tested when a bore is first established and the data is held in the DLRM database. Historical NO<sub>3</sub> data were available for most of the sites and were collected between 1968 and 2000.

## **4. Results**

### **4.1. General water quality**

The general water quality of the 27 sites was very similar across the study area. The ionic composition of groundwater samples depends on the geology of their source aquifer. Samples from the same aquifer are expected to have similar proportions of anions and cations. The bores and springs sampled for this study were selected to be representative of the Tindall limestone aquifer, accordingly, the ionic composition of waters from the bores was very similar, confirming that they are of the same water type and hydrogeological source. The limestone waters of the Tindall aquifer are calcium and magnesium bicarbonate dominated with only small amounts of sodium, chloride and sulphate present in the samples. (Figure 4).

The mean electrical conductivity was 608, with slightly alkaline pH values between 7.7 and 8.5. Alkalinity ranged from 269 to 482 mg/L. Where results were below the limit of reporting (LOR), half the LOR was used in calculations of summary statistics. A summary of general water quality parameters is provided in Table 1 and raw results are presented in Appendix B.



**Figure 4. Piper plot of ionic composition of sampled bores. Samples with similar water types plot close together. Each dot represents one sample.**

**Table 1. Summary statistics of general water quality parameters in bores and springs in the Tindall aquifer Katherine (n=27).**

Parameter (unit)	Mean	(SE)	Min	Max	Median
<b>Field Measurements</b>					
DO (mg/L)	1.9	(0.32)	0.1	6.1	1.5
EC (µS/cm)	692	(12.0)	605	903	683
Field pH* (units)			6.09	7.04	6.58
Temperature (deg C)	31.5	(0.40)	28.9	39.5	31.2
Turbidity (NTU)	0.5	(0.21)	0.1	3.3	0.2
<b>Sample results</b>					
Alkalinity (mg CaCO <sub>3</sub> /L)	362	(9.0)	269	482	365
Ca (mg/L)	90	(2.5)	61	127	87
Cl (mg/L)	8.5	(0.89)	3	20	6.5
CO <sub>3</sub> (mg/L)	1.7	(0.50)	0.5	11	0.5
EC (µS/cm)	608	(14.6)	360	771	623
Hardness	376	(6.5)	303	470	375
HCO <sub>3</sub> (mg/L)	360	(9.3)	260	482	365
K (mg/L)	2.3	(0.21)	0.9	4.8	1.8
Mg (mg/L)	37	(0.90)	25	46	38
Na (mg/L)	7.4	(0.62)	3.4	17	6.4
OH (mg/L)	0.5	(0.00)	0.5	0.5	0.5
Lab pH*			7.7	8.5	8.3
Si (mg/L)	13	(0.49)	8.6	17.4	13
SO <sub>4</sub> (mg/L)	3.9	(0.93)	1.1	25.8	2.5
TDS (mg/L)	381	(5.9)	320	460	380

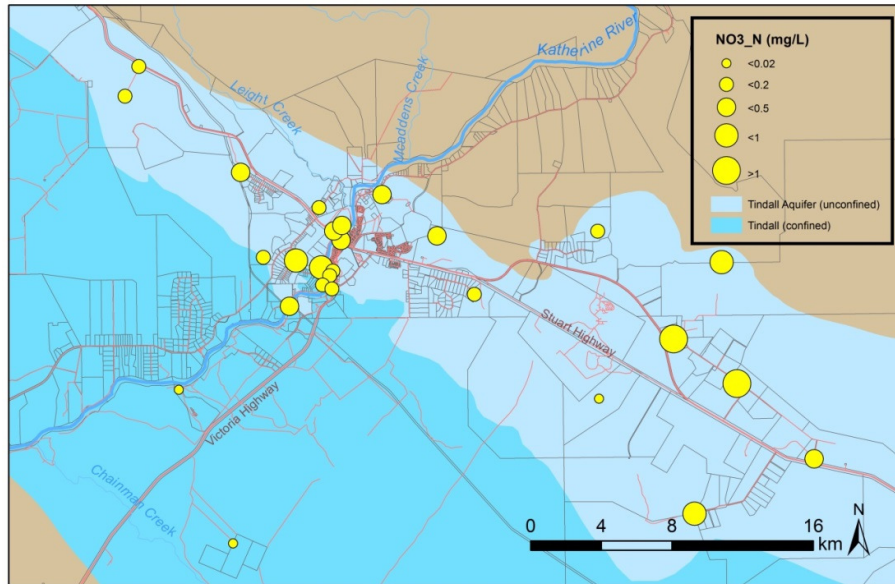
\*pH data unsuitable for calculation of mean due to log<sub>10</sub> scale of pH units

#### 4.1. Nutrients

Soluble nutrient concentrations were low for nitrite (NO<sub>2</sub>), ammonia (NH<sub>3</sub>) and filterable reactive phosphorus (FRP), ranging from <0.001 to 0.006 mg N/L for nitrite, <0.001 to 0.039 mg N/L for ammonia and 0.003 to 0.027 mg P/l for FRP. Nitrate concentrations were more variable across the aquifer and much higher with a mean of 0.350 mg/L and values ranging from <0.001 mg/L to 1.85 mg/L (Figure 5). Total nitrogen concentrations reflected the NO<sub>3</sub> results, with values between 0.02 and 1.88 mg/L, while total phosphorus ranged from 0.006 to 0.047 mg/L (Table 2).

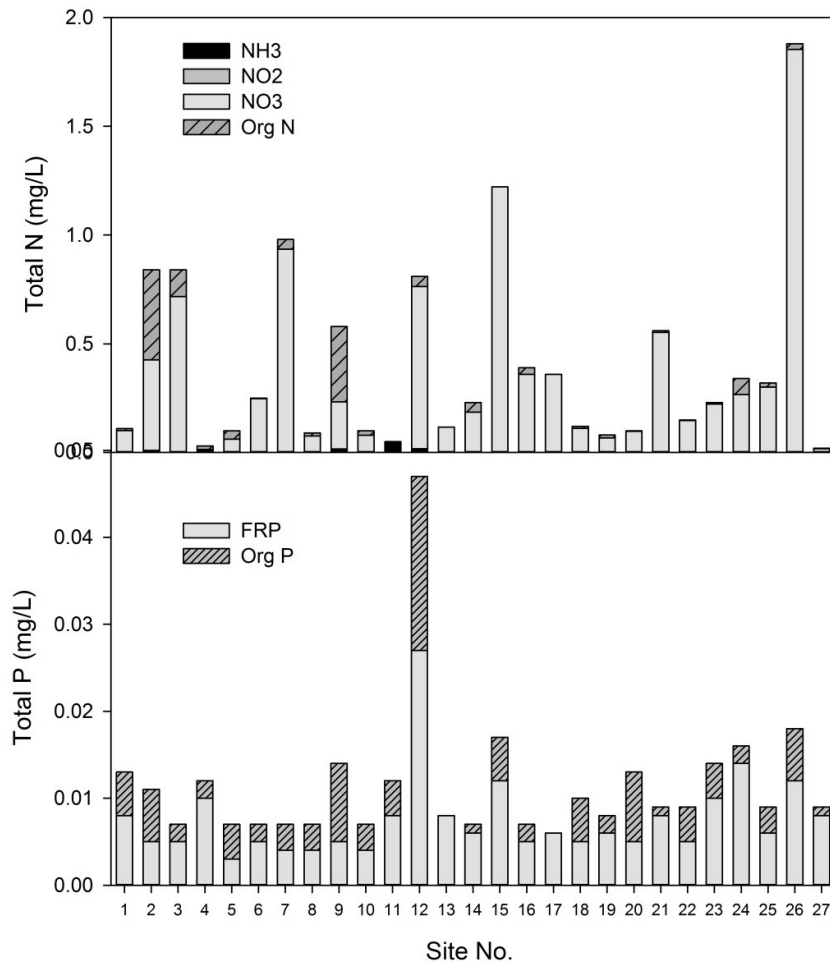
**Table 2. Summary statistics for nutrient concentrations in bores and springs of the Tindall aquifer Katherine (n=27). SE: standard error of the mean.**

Parameter (unit)	Mean	SE	Min	Max	Median
NH <sub>3</sub> _N (mg/L)	0.004	(0.002)	0.001	0.039	0.001
NO <sub>2</sub> _N (mg/L)	0.002	(0.000)	0.001	0.006	0.001
NO <sub>3</sub> _N (mg/L)	0.350	(0.082)	0.001	1.850	0.217
FRP (mg/L)	0.008	(0.001)	0.003	0.027	0.006
TN (mg/L)	0.403	(0.085)	0.020	1.88	0.230
TP (mg/L)	0.011	(0.002)	0.006	0.047	0.009



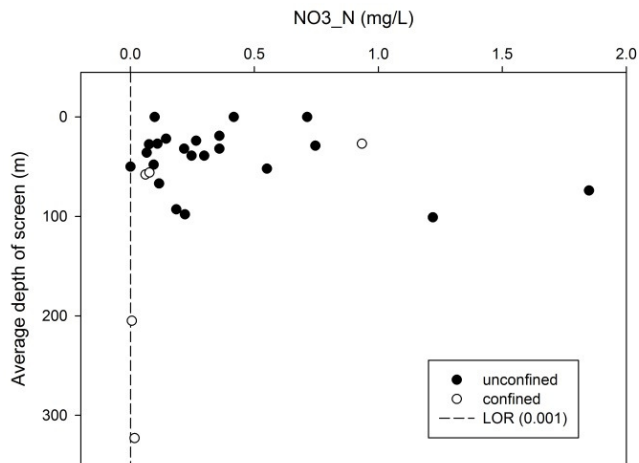
**Figure 5. NO<sub>3</sub> concentrations in bores and springs of the Tindall aquifer.**

Nitrate contributed by far the largest proportion of total nitrogen (mean 80%, SE 5%) with the organic fraction being small in all but 2 samples. With an average of 68% ( $\pm 4\%$ ) soluble phosphorus also contributed the majority of total phosphorus in the samples (Figure 6).



**Figure 6. Contribution of soluble and organic fractions to Total N and Total P concentrations in springs (sites 1-3) and bores of the Tindall aquifer, Katherine.**

There was no significant relationship of nitrate concentration with the depth of the bore slots or nitrate and whether the bore was in the confined or unconfined part of the aquifer (Figure 7). Although bores in the confined section of the aquifer had a much lower median NO<sub>3</sub> concentration (0.06 mg/L) than those within the unconfined area (0.23 mg/L) the difference was not statistically significant due to the small sample size and one outlier with very high NO<sub>3</sub> in the confined group (Mann-Whitney Rank Sum test,  $p > 0.07$ ).



**Figure 7. NO<sub>3</sub> concentration vs average depth of the bore screen in the confined and unconfined sections of the Tindall aquifer. LOR: limit of reporting.**

Median nitrate concentrations ranged from 0.10 mg/L in urban areas to 0.30 mg/L in agricultural areas (Table 3) but differences were not statistically significant due to the large variability in the data (Kruskal-Wallis analysis of variance,  $p > 0.6$ ).

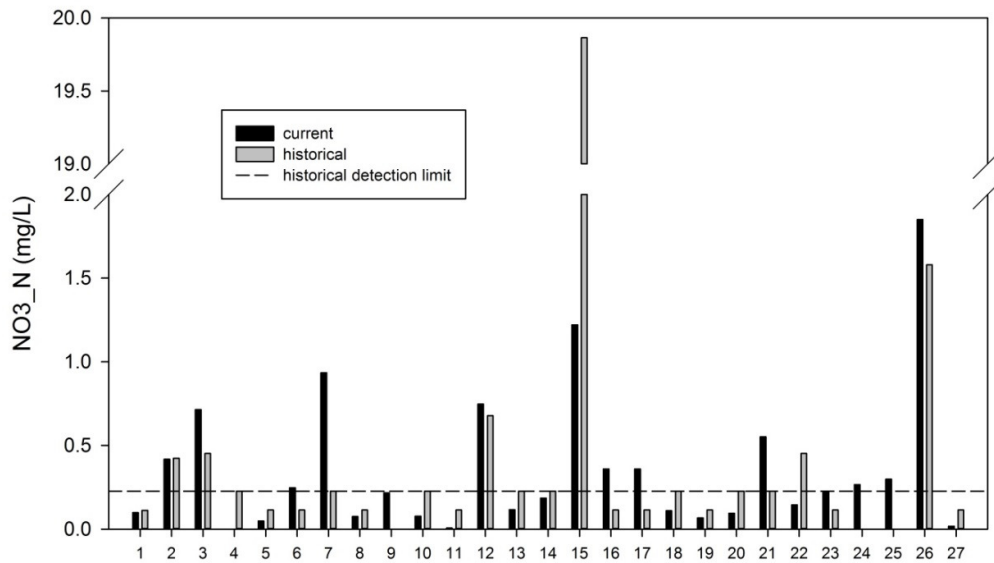
**Table 3. NO<sub>3</sub> (mg N/L) concentrations by land use category**

Land Use Category	n	Median	Mean (SE)	Max	Min
Agriculture	7	0.30	0.60 (0.26)	1.85	0.017
Industrial/urban	6	0.10	0.16 (0.05)	0.75	0.061
Natural environments	6	0.27	0.35 (0.13)	0.93	<0.001
Rural/domestic	8	0.22	0.28 (0.10)	0.93	0.006

A comparison of historical and current NO<sub>3</sub> concentrations in groundwater of the Tindall aquifer is confounded by the fact that although historical bore samples were routinely tested for NO<sub>3</sub>, the detection limit that applied to those samples is much higher than that used for the current survey (1 mg NO<sub>3</sub>/L or 0.26 mg N/L vs. 0.001 mg N/L).

Nevertheless, a comparison of the current results with historical data reveals that many of the sites with the highest NO<sub>3</sub> concentrations today had high NO<sub>3</sub> concentrations in the past (Figure 8). Approximately one third of sites had current NO<sub>3</sub> concentrations that were higher than those measured in the past.

This comparison should only be considered an indication since in most cases only one single historical and one current measurement are available.



**Figure 8. Comparison of historical (1968-2000) and current NO<sub>3</sub> concentrations in Tindall aquifer springs (sites 1-3) and bores.** Where concentrations were below the detection limit, half the detection limit is shown.

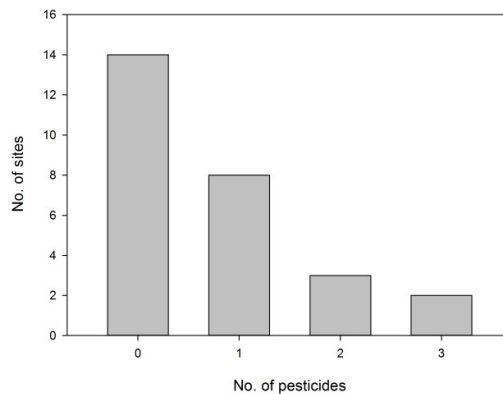
#### 4.2. Pesticides and Herbicides

Of 27 sites, 14 had no detections of any pesticides or herbicides (Figure 9. Frequency of pesticide detection. Figure 9). In the remaining 13 sites, seven different pesticides and herbicides and/or their breakdown products were found in samples from a least one site. No more than three different herbicides or pesticides were found at any one site (Figure 9). None of the detected pesticides or herbicides exceeded guideline values for moderately disturbed ecosystems (ANZECC 2000).

The most commonly detected chemicals were the herbicide *atrazine* and its breakdown products *desethyl atrazine* and *desisopropyl atrazine*, with some form of atrazine residues detected in 2 springs and 8 bores.

The herbicides *tebuthiuron* and *simazine*, both triazine herbicides of a similar chemical class to atrazine, were found at 3 and 2 sites respectively.

*Imidacloprid*, an insecticide, and its breakdown products, were found at 2 sites, while the herbicides *haloxyfop* and *imazapyr* and the UV stabiliser compound *2,4-di-t-butylphenol* were only detected at a single site each (Table 4). Raw results are presented in Appendix C.



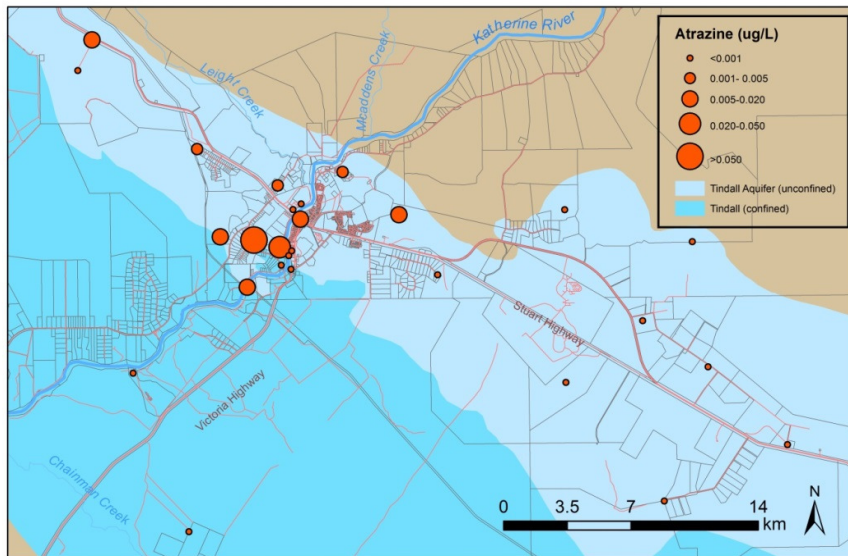
**Figure 9. Frequency of pesticide detection.**



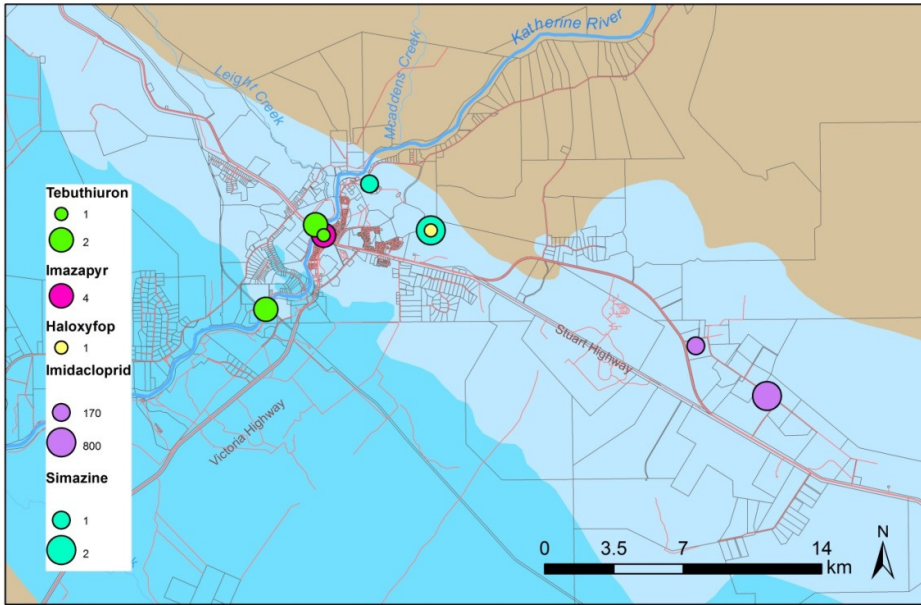
**Table 4. Results of pesticide analysis for Tindall aquifer groundwater, 2015. Only detected pesticides are listed.**

Analyte	ANZECC Guideline (µg/L)	Detection Limit (µg/L)	% detection (No. of sites)	Concentration (µg/L)	
				Mean	Max
<b>Herbicides</b>					
Atrazine	13	0.001	29 (8)	0.003	0.007
Desethyl atrazine	-	0.001	37(10)	0.013	0.059
Desisopropyl atrazine	-	0.001	33 (9)	0.007	0.024
Tebuthiuron	2.2	0.001	11 (3)	0.002	0.002
Simazine	3.2	0.001	7 (2)	0.002	0.002
Haloxypop	-	0.001	4 (1)	0.001	0.001
Imazapyr	-	0.001	4 (1)	0.004	0.004
<b>Insecticides</b>					
Total Imidacloprid	-	0.003	7 (2)	0.485	0.800
<b>Other chemicals</b>					
2,4-di-t-butylphenol	-	0.1	4 (1)	1.3	1.3

For further analysis, the concentrations of atrazine and its two break-down products desethyl atrazine and desisopropyl atrazine were added and treated as “total atrazine residues”. Figure 10 and Figure 11 show the concentrations of combined atrazine residues and other herbicides and pesticides across the study area. No atrazine residues were detected in the south-eastern part of the study area.

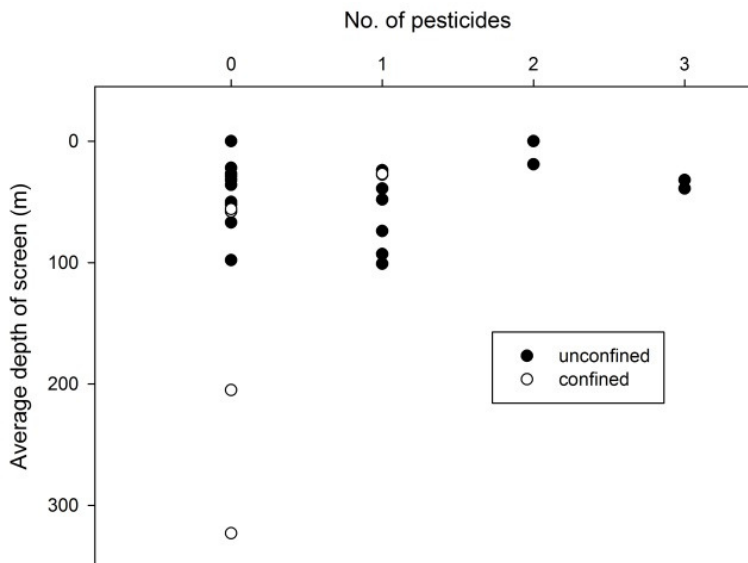


**Figure 10. Concentrations (µg/L) of atrazine and its breakdown products combined, in bores and springs of the Tindall aquifer, Katherine.**

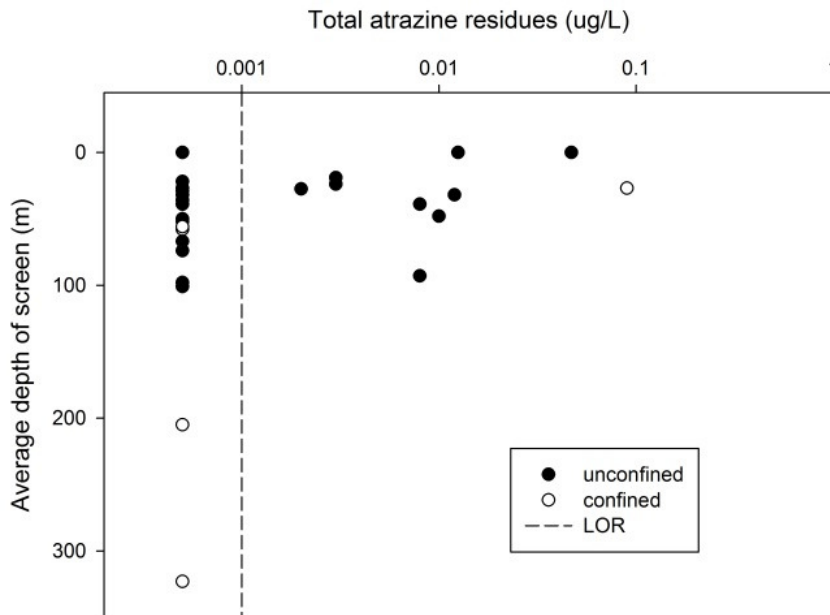


**Figure 11. Concentrations (ng/L) of other pesticides in bores and springs of the Tindall aquifer, Katherine. Only bores where pesticides were detected are shown.**

Pesticide and herbicide residues were detected in both shallow and deeper bores of the unconfined part of the aquifer (Figure 12). In the confined section only one herbicide (atrazine) was detected in the shallowest bore. The highest atrazine concentrations were found in shallow unconfined bores (Figure 13).

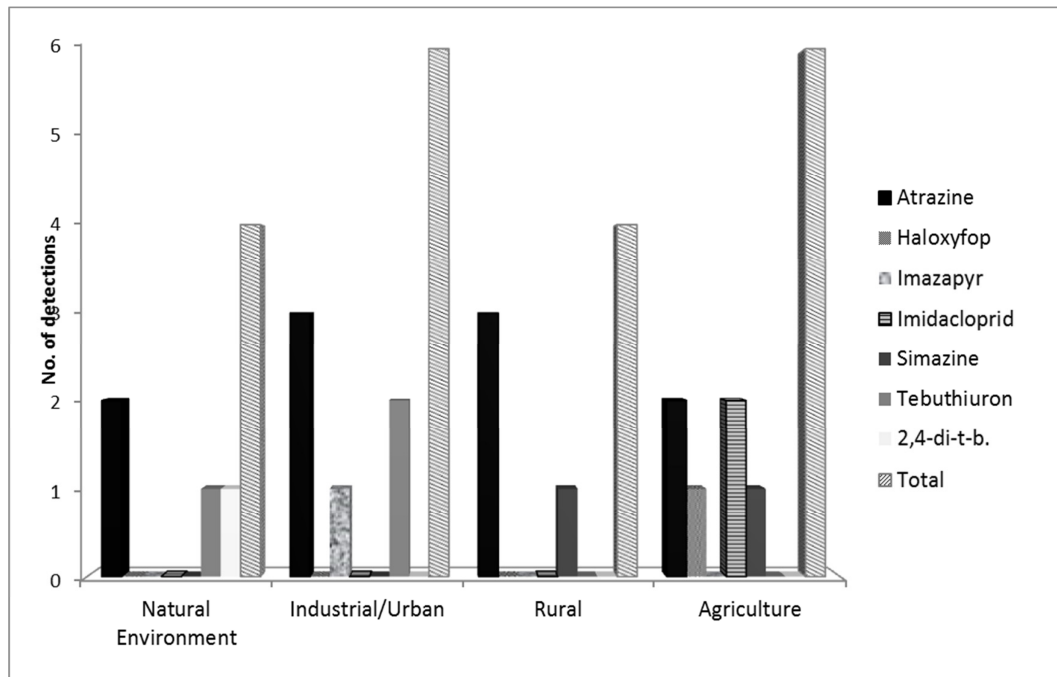


**Figure 12. Number of pesticides detected in bores of the confined and unconfined sections of the Katherine Tindall aquifer**



**Figure 13. Atrazine residue concentration (note: log scale) in bores of the confined and unconfined sections of the Katherine Tindall aquifer. LOR: limit of reporting**

Herbicides and/or pesticides were detected under all land uses. The highest number of detections occurred in the industrial/urban and agricultural categories (Figure 14).



**Figure 14. Number of detections of each herbicide/pesticide by land use.**

Atrazine residues were found in all land use categories. The median combined atrazine concentration was below the detection limit of 0.001 µg/L for all land uses except industrial/urban land use, which had a median of 0.001 µg/L (Table 5). Differences between land uses were not statistically significant (Kruskal-Wallis analysis of variance,  $p > 0.9$ ). However, the highest individual concentrations of atrazine were found in areas of rural land use and natural environments.

**Table 5. Total atrazine residue concentration in different land use categories.**

Land Use Category	n	# of detections	Median	Mean (SE)	Max	Min
Agriculture	7	2	<0.001	0.003 (0.0014)	0.008	<0.001
Industrial/urban	6	3	0.001	0.004 (0.0022)	0.012	<0.001
Natural environments	6	2	<0.001	0.010 (0.0076)	0.047	<0.001
Rural/domestic	8	3	<0.001	0.012 (0.011)	0.090	<0.001

## 5. Discussion

### 5.1. Nitrate

Nitrate concentrations within the Tindall aquifer are low in comparison to other regions of Australia where concentrations of up to 50 mg<sub>N</sub>/L have been found in groundwater (Bolger and Stevens 1999). However, the high variability in nitrate concentrations from less than 0.001 mg<sub>N</sub>/L to nearly 2 mg<sub>N</sub>/L indicates that nitrate concentrations are influenced by local surface processes.

The highest concentrations of nitrate were detected in the agricultural area of the “Venn subdivision”, southeast of the town of Katherine. Intensive agricultural land use and the application of fertilisers and manures is one of the most common sources of nitrate in groundwater throughout the world (Bolger and Stevens 1999). A review by Geoscience Australia (Sundaram and Coram 2009) found that elevated nitrate concentrations in Australia were generally found in areas surrounded by intensive agriculture.

In the Australian arid zone, nitrogen-fixing bacteria associated with termites have been identified as a major potential natural source of nitrate to groundwater (Barnes et al. 1992). While termite activity cannot be discounted as a source of nitrate in the Tindall aquifer, termites are unlikely to be major nitrate contributors in agricultural areas.

The comparison with historical data from the Katherine region shows that the highest current nitrate concentrations were associated with high historical levels. In some bores, concentrations appear to have fallen since the 1970s when much higher concentrations were measured in the same bores. However, a number of sites had increased nitrate concentrations compared to historical samples. More intensive time series monitoring would be required to establish reliable temporal trends since there can be substantial variation in nitrate concentrations from any one location over time (e.g. EPA WA 1991, 1993 cited in Bolger and Stevens 1999)

With the exception of one site, nitrate levels were lower in bores in the confined sections of the aquifer where there is no direct connection between the surface and the aquifer storage within the Tindall limestone. Only one site had a high concentration of nitrate despite being located in the confined area. This site is located on the edge of the confined and unconfined parts of the aquifer where the confining layer of the Jinduckin Formation is thin. There may still be some connectivity between the surface and the limestone aquifer or “downstream” movement of water from the nearby unconfined area may be affecting the water quality in this bore.

The effect of the elevated groundwater nitrate concentrations on the health of the Katherine River has not been well studied. Water quality studies of the Katherine River have previously noted the increased nitrogen inputs to the river from Tindall aquifer spring inflows (e.g. Lawrie 2014, Schult 2011, and unpublished NTG data) but there is no apparent change in the river’s ecology. The increased nutrients are taken up quickly by biological processes in the river, apparently without resulting in a significant increase of nuisance algae or a change in plant biodiversity (pers. obs.). A factor contributing to this lack of impact may be the low phosphorus levels in the river and the Tindall groundwater which may limit algal growth even where nitrate is plentiful.

At very high concentrations nitrate in drinking water can be a human health concern, especially where water is used to prepare infant food. The concentrations found in groundwater in this study were all below the national drinking water guideline value for infants of 11 mg\_N/L (NHMRC 2011).

## **5.2. Pesticides and herbicides**

Pesticides and herbicides are an integral part of modern agricultural practices. With the widespread use of these chemicals it is almost inevitable that traces of them will make their way into the environment.

The results of the groundwater quality survey show that there is currently very little contamination of waters of the Tindall aquifer with pesticides or herbicides. Only seven different herbicides or pesticides and their derivatives were detected out of a total of approximately 180 substances that were tested for. All of the detected chemicals were found at very low concentrations that would mostly have been undetectable prior to recent improvements to analytical methods. None of the samples exceeded environmental or drinking water guidelines.

Table 6 provides a brief description of some of the uses and properties of the chemicals that were detected in this study.

**Table 6.** Description of chemicals detected in Katherine Tindall bores and springs

<b>Chemical name</b>	<b>Description</b>	<b>Examples of trade names</b>
<i>2,4-Di-t-butylphenol</i>	Compound used in the manufacture of UV stabilizers and anti-oxidants. Toxic to freshwater fish in higher doses (LC50:1.8mg/L) (PubCRIS 2016)	N/A
<b>Atrazine</b>	Atrazine is one of the main herbicides used in Australia. Used before and after planting of crops to control broad-leaved weeds and grasses in crops such as sorghum, sugar cane, maize and canola. Also used in turf and non-agricultural sites such as lawns, industrial areas, rights-of-way and in orchards (APVMA 2008, US EPA 2014). Atrazine is a common contaminant of surface and groundwater in Eastern Australia (Shaw and Muller 2005) and has been banned in Europe after persistent contamination of groundwater was found (European Commission 2014)	Farmozine Nutrazine Gesaprim
<i>Desethyl Atrazine</i>	Breakdown product of atrazine	N/A
<i>Desisopropyl Atrazine</i>	Breakdown product of atrazine	N/A
<b>Haloxypop (acid)</b>	Herbicide for the control of annual and perennial grasses in legume, oilseed and pasture crops, tropical fruits and nuts. (PubCris 2016).	Wellfarm Haloxypop Jasper 520 Relyon Citrus 520
<b>Imazapyr</b>	Herbicide for the control of grasses and broadleaved herbs. Registered for the use in agricultural non-crop areas, rights of way, commercial and industrial areas (APVMA)	Farmalinx Bomber Aureo 250 Conquest Gunner
<b>Imidacloprid</b>	Very commonly used systemic insecticide of the neonicotinoid class. Used on trees to control insect pests, and domestically to control termites, ants and cockroaches. High leachate risk. Highly toxic to aquatic invertebrates at higher concentrations than those found in this study.	Confidor Premis
<i>Imidacloprid metabolites</i>	Breakdown products of imidacloprid	N/A
<i>Total Imidacloprid</i>	Sum of imidacloprid and its metabolites	N/A
<b>Simazine</b>	Systemic triazine herbicide. Absorbed through roots. Stable in water, decomposed by UV light, binds to soil. Controls broad-leaf weeds in a variety of crops and at higher rates of application, grasses and broad-leaved weeds in other areas. Used in citrus and for non-crop weed control on roads, railways etc. High risk of groundwater leaching.	Accensi
<b>Tebuthiuron</b>	A general herbicide that is commonly used to control weeds. It is slightly toxic to aquatic vertebrates and invertebrates at higher concentrations but has little potential to accumulate in the environment.	Farmalinx Graslan Tebulan

The most commonly detected contaminant was the herbicide atrazine. Atrazine and its breakdown products were detected at 37% of sites. Atrazine is known to be a common contaminant of groundwater due to its widespread use and high mobility (APVMA 2008). With a maximum of 0.059 µg/L of desethyl atrazine, concentrations of atrazine and its breakdown products in the Tindall aquifer were relatively low compared to a recent (2011) study from the Burdekin region in Queensland where concentrations of desethyl atrazine of up to 0.254 µg/L were found in local groundwater (Shaw et al. 2012). Even higher levels of up to 1.4 µg/L were detected in the same region in 1992-93 (Bauld et al. 1996, cited in Shaw et al. 2012).

Prior to 1999 atrazine products were approved for general use on lawns, roadsides, industrial areas and drains. A review by the APVMA concluded that these uses contributed significantly to the total environmental load of atrazine and thus such uses should not be continued (APVMA 2008). Atrazine is now only approved for agricultural use in Australia with the exception of the control of parthenum weed. Consequently, levels of atrazine contamination are expected to decline in the future. In our study, atrazine was detected under all land uses although it was notably absent at the sites of the most intensive agriculture.

Atrazine is considered highly persistent in soil (Cheminova 2014) and is broken down in the environment by light and soil microbes. Giddings et al. (2005) conducted a review of studies of atrazine breakdown. They found few studies on the persistence of atrazine in groundwater or on the persistence of atrazine breakdown products such as desethyl atrazine; however, a number of studies have measured atrazine breakdown in soils and surface water and found varying results. Under anaerobic (water-logged) soil conditions the half-life for atrazine (the time it takes for half the initial atrazine concentration to be broken down) was 58-547 days, while a half-life of between 1 and 355 days was found in surface freshwater. Breakdown times depend on environmental conditions such as soil type, presence of organic material, pH and the wavelength of the light as well as the microbial community present. Breakdown occurred faster under acidic or alkaline conditions.

The variability in results and the lack of studies investigating persistence of atrazine in groundwater means that no reliable estimate of the age of the current contamination can be made. Once atrazine reaches the aquifer, it is likely to persist longer than in soil or surface water due to the lack of light and the anaerobic conditions that prevail.

All other herbicides and pesticides that were detected in this study were found in very few samples (3 or less). No spatial patterns of contamination could be discerned due to the small number of detections. However, for two of the chemicals (simazine and imidacloprid), both were detected in two sites close to each other, with the lower concentration in the bores that were located “downstream” of the groundwater flow direction. This may suggest that the contamination originated from “upstream” bores and moved from there towards the “downstream” sites with the natural groundwater flow. Contamination appears to be localised and might have occurred due to inappropriate application or storage of chemicals at individual sites.

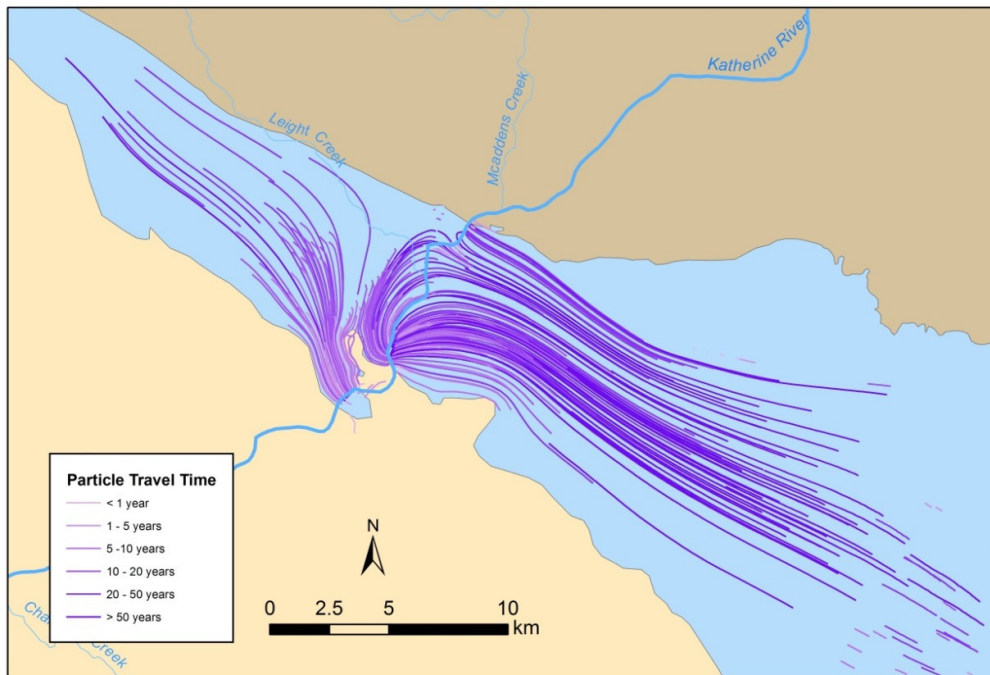
### 5.3. Groundwater Modelling and Age Analysis

The time it takes for groundwater to move through the aquifer to discharge points in the landscape is difficult to predict. Flows in karst aquifers like the Tindall can be highly variable due to the cavernous and fractured nature of the limestone rock. Dye tracing experiments in the Katherine area found that a non-toxic dye poured into a sinkhole could be detected in some bores and springs several kilometres away within days (Karp 2005). Groundwater that enters the aquifer in other regions or further away from discharge areas of the river may take years, decades or more to reach discharge zones.

There are several processes which affect the fate and persistence of contaminants in the natural environment. Specific contaminant transport modelling would be needed to determine the fate of contaminants in the study area with more certainty. For the purpose of this report, the flow rate and pathlines taken by groundwater can be regarded as a general indicator of the travel pattern of potential contaminants through the aquifer.

A three dimensional finite element groundwater model (FEFLOW) coupled to a channel flow model (Mike11) has been developed for the Daly Basin (Knapton,2011). This model was used to predict groundwater flow under natural conditions within the Tindall Limestone Aquifer over the period 1900 – 2016. Reverse particle tracking analysis was used to identify groundwater flowpaths and travel times through the study area.

The results show average travel times of approximately 0.2-1km/year in the unconfined part of the Tindall aquifer. Faster flow rates occur along the southern edge of the aquifer where it discharges into the Katherine River (Figure 15). The aquifer is confined by the overlying Jinduckin Formation to the south which restricts entry of particles into the saturated, pressurised component of the aquifer.



**Figure 15. Modelled particle travel time in the Tindall aquifer to reach the Katherine River under current pumping conditions.**



The results of the reverse particle tracking indicate that groundwater particles found in the river will have taken between 3 months and more than 50 years to reach the river, depending on the location of their source (Figure 15). Where deeper layers of the aquifer are affected, particles can also move under the river bed, indicating that in some cases groundwater particles that enter the river discharge zone from the western bank can potentially originate from regions to the eastern of the river.

Ageing of groundwater using carbon dating techniques undertaken in parallel to this study confirmed that the unconfined aquifer contains, at least in part, more recent waters (<50 years), while water from the confined aquifer is much older and contains little recent recharge (Tickell 2016). The carbon dating study also indicates that there is little movement of water from the unconfined recharge zone to the confined part of the aquifer with movement occurring mainly parallel to the edges of the Tindall aquifer. Waters older than 100 years are unlikely to contain pesticides, since these were only introduced widely from about the 1940s.

To trace the exact origin and age of the aquifer water and the selected compounds a much more detailed investigation would be required.

Dry season surface water sampling of the Katherine River in 2011 detected some of the same compounds that were found in groundwater in the current study. The highest concentrations of the triazine herbicides atrazine, tebuthiuron and simazine found in surface water were much lower than the concentrations found in some of the bores (Table 7).

Sampling techniques differed between the two studies. For surface water samples, individual sample concentrations represent an estimated flow-weighted average concentration over 4 weeks of chemical accumulation at a site (see Schult 2012 for detailed methods). The river water maximum shown in Table 7 is the highest flow-weighted average concentration found at any one site.

**Table 7. Comparison between maximum measured groundwater and surface water chemical concentrations in the Katherine region.** (NS: not sampled, ND: not detected).

Analyte	2015	2011
	Groundwater max (ng/L)*	River Water max (ng/L)*
Atrazine	7	0.39
Atrazine desethyl	59	1.48
Atrazine desisopropyl	24	NS
Tebuthiuron	2	0.38
Simazine	2	0.11
Haloxfop	1	ND
Imazapyr	4	NS
Imidacloprid	800	NS
2,4-di-t-butylphenol	1300	NS
Chlorpyrifos	ND	0.6
Methamidaphos	NS	42
DEET	ND	189
Galaxolide	ND	22.3

Tonalide	ND	6.2
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(Surface water data from Schult 2012)

Surface water concentrations are expected to be lower since the river flows are comprised of a mixture of waters from the Cretaceous sandstone aquifer and a mix of water from different areas of the Tindall aquifer. Since herbicides were not present at all sites within the Tindall Limestone, a dilution effect is expected from affected and unaffected sections of the aquifer.

Other compounds were found in the surface water but not in groundwater. Some of these are likely to originate from recreational use of waterways and included the mosquito repellent DEET and the fragrances tonalid and galaxolide, that are common in personal care products such as sunscreens and lotions.

Some of the substances found in this study were not included in the suite of chemicals tested in the previous surface water study and vice versa because different sampling techniques were used in the two studies. For any future monitoring of surface water these compounds should be included in the suite of analytes to establish whether they have travelled to and reached the discharge areas.

## 6. Conclusion

This survey was the first comprehensive study of groundwater quality in the Tindall aquifer. The impact of human activities in the Katherine region on the water quality of the Tindall aquifer is currently small. There is some localised low level contamination of the aquifer with nitrate which is likely to be caused at least in part by human activities, including agricultural land use. Contamination of the local groundwater with pesticides and herbicides has also occurred infrequently at low levels, with the exception of the herbicide atrazine which is fairly widespread with residues present in 37% of samples. The time for pesticide and herbicide contaminated groundwater travel to the Katherine River from the survey area is uncertain, owing to the potentially wide range of modelled travel times and unknown rates of degradation. A comparison with dry season river water concentrations suggests the groundwater contamination is diluted by both uncontaminated groundwater and Cretaceous sandstone groundwater-fed river flow.

The concentrations of both nitrate and pesticide contaminants are currently well below guidelines for health and environmental protection and are low in comparison with many other regions of Australia. However, any detection of aquifer contamination should serve as a reminder to apply best practice in the storage, application and disposal of any domestic and agricultural chemicals.

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## Appendix A: List of analytes for pesticide/herbicide analysis

ID	Description	LoR (µg/L)	ANZECC	ADWG	ID	Description	LoR (µg/L)	ANZECC	ADWG
<b>Herbs GCMS All</b>					KEENDE	Endosulfan ether (OC)	0.1		--
KE34DA	3,4-Dichloroaniline	0.1		--	KEENDL	Endosulfan lactone (OC)	0.5		--
KEAM1	Ametryn (HBG)	0.1		70	KEENDS	Endosulfan sulfate (OC)	0.1		20
KEAMIT	Amitraz (HBG)	0.1		9	KEERIN	Endrin (OC)	0.2		--
KEATR1	Atrazine (HBG)	0.1		20	KEERIA	Endrin aldehyde (OC)	0.1		--
KEBROM	Bromacil (HBG)	0.1		400	KEHCB	HCB (OC)	0.2		--
KEDZ1	Desethyl Atrazine (HBG)	0.1		--	KEHCHA	HCH alpha (OC)	0.1		--
KEDOZ1	Desisopropyl Atrazine (HBG)	0.1		--	KEHCHB	HCH beta (OC)	0.1		--
KEDICM	Diclofop-methyl (HBG)	0.1		5	KEHCHD	HCH delta (OC)	0.1		--
KEFLZF	Fluazifop-butyl (HBG)	0.1		--	KECBH	Heptachlor (OC)	0.1		0.3
KEFLM1	Fluometuron (HBG)	0.1		70	KECBHE	Heptachlor epoxide (OC)	0.1		0.3
KEHO2E	Haloxypop-2-etotyl (HBG)	0.1		1	KEELD	Lindane (OC)	0.1		10
KEHOM	Haloxypop-methyl (HBG)	0.1		1	KEMET	Methoxychlor (OC)	0.1		300
KEHZ1	Hexazinone (HBG)	0.1		400	KENONC	Nonachlor cis (OC)	0.1		--
KEMETC	Metolachlor (HBG)	0.1		300	KENONT	Nonachlor trans (OC)	0.1		--
KEMRB	Metribuzin (HBG)	0.1		70	KEODDD	o-p DDD (OC)	0.1		--
KEMOLN	Molinate (HBG)	0.1		4	KEODDE	o-p DDE (OC)	0.1		--
	<b>Organics Env. Lab #</b>			--	KEODDT	o-p DDT (OC)	0.1		9
KEOXYF	Oxyfluorfen (HBG)	0.1		--	KELN	Organics Env. Lab #			--
KEPDM	Pendimethalin (HBG)	0.1		400	KEOXC	Oxychlordan (OC)	0.1		2
KEPM1	Prometryn (HBG)	0.1		--	KEPDDD	p-p DDD (OC)	0.1		9
KEPPNL	Propanil (HBG)	0.1		700	KEPDDE	p-p DDE (OC)	0.1		9
KEPPZN	Propazine (HBG)	0.1		50	KEPDDT	p-p DDT (OC)	0.1		9
KESM1	Simazine (HBG)	0.1		20	KETAD	Total Aldrin & Dieldrin (OC)	0.2		0.3
KETB1	Tebuthiuron (HBG)	0.1		--	KEDDT	Total DDT (OC)	0.4		9
KETBTZ	Terbuthylazine (HBG)	0.1		10	KEEND	Total Endosulfan (OC)	0.6		20
KETBTY	Terbutryn (HBG)	0.1		400	KETHC	Total Heptachlor (OC)	0.2		0.3
KETRIA	Triallate (HBG)	0.1		--	<b>Organophosphate Pesticides</b>				
KETRIF	Trifluralin (HBG)	0.1		90	KEAZPE	Azinphos-ethyl (OP)	0.1		--
KEALD	Aldrin (OC)	0.1		0.3	KEAZPM	Azinphos-methyl (OP)	0.1		30
KECLDC	Chlordane cis (OC)	0.1		2	KEBMPE	Bromophos-ethyl (OP)	0.1		10
KECLT	Chlordane Total (OC)	0.2		2	KECADS	Cadusafos (OP)	0.1		--
KECLDT	Chlordane trans (OC)	0.1		2	KECARP	Carbophenothion (OP)	0.1		0.5
KECHL	Chlordene (OC)	0.1		--	KECHFV	Chlorfenvinphos (OP)	0.1		2
KECHLE	Chlordene epoxide (OC)	0.1		--	KECHP	Chlorpyrifos (OP)	0.1		10
KEC1H	Chlordene-1-hydroxy (OC)	0.1		--	KECHPO	Chlorpyrifos oxon (OP)	0.1		--
KEC1H2	Chlordene-1-hydroxy-2,3-epoxide (OC)	0.1		--	KECHPM	Chlorpyrifos-methyl (OP)	0.1		--
KEDIC	Dicofol (OC)	1.5		4	KECOUM	Coumaphos (OP)	0.1		--
KEDIEL	Dieldrin (OC) new	0.1		0.3	KEDEOM	Demeton-O-methyl	0.1		--
KEENDA	Endosulfan Alpha (OC)	0.2		20	KEDEMT	Demeton-S 16315	0.1		--
KEENDB	Endosulfan Beta (OC)	0.2		20	KEDESM	Demeton-S-methyl (OP)	0.1		--
					KEDIAZ	Diazinon (OP)	0.1		4
					KEDICH	Dichlorvos (OP)	0.1		5
					KEDIME	Dimethoate (OP)	0.1		7

ID	Description	LoR (µg/L)	ANZECC	ADWG	ID	Description	LoR (µg/L)	ANZECC	ADWG
KEDIOX	Dioxathion (OP)	0.1		--	KENBBS	N-Butylbenzenesulfonamide (OTCG)	0.1		--
KEDIS	Disulfoton (OP)	0.1		4	KENBTS	N-Butyltoluenesulfonamide (OTCG)	0.1		--
KEETHI	Ethion (OP)	0.1		4		<b>Organics Env. Lab #</b>			--
KEETHP	Ethoprophos (OP)	0.1		1	KETONL	Tonalid (OTCG)	0.1		--
KEETRI	Etrimphos (OP)	0.1		--	KETNBP	Tri-n-butyl phosphate (OTCG)	0.1		--
KEFAMP	Famphur (OP)	0.1		--	KETRIC	Triclosan (OTCG)	0.1		--
KEFENA	Fenamiphos (OP)	0.1		0.5	KETCME	Triclosan methyl ether (OTCG)	0.1		--
KEFENC	Fenchlorphos (OP)	0.1		30	KETEP	Triethyl phosphate (OTCG)	0.1		--
KEFENI	Fenitrothion (OP)	0.1		7	KETCEP	Tris(chloroethyl) phosphate (OTCG)	0.1		--
KEFENM	Fenthion (methly) (OP)	0.1		7	KETCPP	Tris(chloropropyl) phosphate isomersOTCG	0.1		--
KEFENE	Fenthion-ethyl (OP)	0.1		--	KETDCP	Tris(dichloropropyl) phosphate (OTCG)	0.1		--
KEISOP	Isofenphos (OP)	0.1		--		<b>Other Pesticides 1</b>			--
KEMALA	Malathion (OP)	0.1		70	KEBENA	Benalaxyl (OTP)	0.1		--
KEMETD	Methidathion (OP)	0.1		6	KEBENC	Bendiocarb (OTP)	0.1		--
KEMEVI	Mevinphos (OP)	0.1		5	KEBITE	Bitertanol (OTP)	0.1		--
KEMCP	Monocrotophos (OP)	0.1		2	KECAPT	Captan (OTP)	0.1		--
KEOME	Omethoate (OP)	0.2		1	KECARB	Carbaryl (OTP)	0.1		400
KEOXDM	Oxydemeton-methyl (OP)	0.1		--	KEDEET	DEET (OTP)	0.1		30
KEPARE	Parathion (ethyl) (OP)	0.1		--	KEDIMM	Dimethomorph (OTP)	0.2		--
KEPARM	Parathion-methyl (OP)	0.1		20	KEWFIP	Fipronil (OTP)	0.1		--
KEPHOR	Phorate (OP)	0.1		0.7	KEFLTF	Flutriafol	0.1		0.7
KEPHOS	Phosmet (OP)	0.1		--	KEFURA	Furalaxyl (OTP)	0.1		--
KEPHOP	Phosphamidon (OP)	0.1		--	KEMLAX	Metalaxyl (OTP)	0.1		--
KEPIRM	Piromiphos-methyl (OP)	0.1		--	KEMETP	Methoprene (OTP)	0.1		--
KEPROF	Profenofos (OP)	0.1		90		<b>Organics Env. Lab #</b>			--
KEPROT	Prothiofos (OP)	0.1		0.3	KEOXAD	Oxadiazon (OTP)	0.1		--
KEPYRZ	Pyrazophos (OP)	0.1		--	KEPIPB	Piperonyl butoxide (OTP)	0.1		--
KESUL	Sulprofos (OP)	0.1		20	KEPIMC	Pirimicarb (OTP)	0.2		600
KETEME	Temephos (OP)	0.1		10	KEPRAQ	Praziquantel	0.1		7
KETERB	Terbufos (OP)	0.1		400	KEPCYM	Procymidone (OTP)	0.1		--
KETCVP	Tetrachlorvinphos (OP)	0.1		1	KEPROG	Propargite (OTP)	0.1		--
KEDIMT	Total Dimethoate (OP)	0.3		100	KEPPIC	Propiconazole (OTP)	0.1		7
KEOTCG	<b>Other Compounds GCMS</b>			7	KEPROX	Propoxur (OTP)	0.1		100
KE1HBZ	1H-Benzotriazole (OTCG)	0.7		--	KEROTN	Rotenone (OTP)	0.1		--
KE1HB1	1H-Benzotriazole, 1-methyl (OTCG)	0.1		--	KETEBU	Tebuconazole (OTP)	0.1		--
KE1HB5	1H-Benzotriazole, 5-methyl (OTCG)	0.2		--	KETDIF	Tetradifon (OTP)	0.1		--
KE24DT	2,4-Di-t-butylphenol	0.1		--	KETHIB	Thiabendazole (OTP)	0.2		--
KEDTBC	2,6-Di-t-butyl-p-cresol (OTCG)	0.1		--	KETTRM	Total Triadimefon (OTP)	0.3		--
KEDTBP	2,6-Di-t-butylphenol (OTCG)	0.3		--	KETRIM	Triadimefon (OTP)	0.1		90
KE2B4C	2-Benzyl-4-chlorophenol	0.2		--	KETRIN	Triadimenol (OTP)	0.1		90
KECDMP	4-Chloro-3,5-dimethylphenol (OTCG)	0.1		--	KEVINC	Vinclozolin (OTP)	0.1		--
KEBESA	Benzenesulfonanilide	0.2		--		<b>Synthetic Pyrethroids 1</b>			--
KEGALA	Galaxolide (OTCG)	0.1		--	KEBIFN	Bifenthrin (SP)	0.1		--
KEICAD	Icaridin	0.1		--	KEBIRM	Bioresmethrin (SP)	0.1		--
KEMOCL	Moclobemide (OTCG)	1		--	KECYFL	Cyfluthrin (SP)	0.1		100
KEMSKK	Musk Ketone (OTCG)	0.1		--	KELAMC	Cyhalothrin (SP)	0.1		50
KEMSKX	Musk Xylene (OTCG)	0.1		--	KECYPM	Cypermethrin (SP)	0.1		--

ID	Description	LoR (µg/L)	ANZECC	ADWG	ID	Description	LoR (µg/L)	ANZECC	ADWG
KEDELM	Deltamethrin (SP)	0.1		200	KHSP53	Metolachlor (low)	0.001		--
KEFENV	Fenvalerate (SP)	0.1		40	KHSP58	Metribuzin (Low)	0.001		--
KEFLUV	Fluvalinate (SP)	0.1		60	KHSP74	Metsulfuron methyl (low)	0.001		--
	<b>Organics Env. Lab #</b>			--	KHSP1F	N-Demethyl Acetamiprid (Low)	0.001		--
KEPERM	Permethrin (SP)	0.1		--	KHSP75	Napropamide (low)	0.001		--
KEPHEN	Phenothrin (SP)	0.1		200		<b>Organics Env. Lab #</b>			--
KETETM	Tetramethrin (SP)	0.1		--	KHSP54	Prometryn (low)	0.001		--
KETRAF	Transfluthrin (SP)	0.1		--	KHSP76	Propachlor (low)	0.001		--
				--	KHSP77	Propazin-2-hydroxy (low)	0.001		--
				--	KHSP78	Sethoxydim (including Clethodim) (low)	0.008		--
	<b>Water Glyphosate LCMS</b>				KHSP55	Simazine (low)	0.001	3.2	--
KEAMPL	Aminomethylphosphonic Acid (AMPA) LL	0.5		--	KHSP79	Sulfosulfuron (low)	0.001		--
KEGLUF	Glufosinate LL	0.5		--	KHSP56	Tebuthiuron (low)	0.001	2.2	--
KEGLYL	Glyphosate LL	0.5		--	KHSP80	Terbuthylazine (low)	0.001		--
KELN	<b>Organics Env. Lab #</b>			--	KHSP81	Terbuthylazine desethyl (low)	0.001		--
KETGLY	Total Glyphosate	1	370	--	KHSP57	Terbutryn (low)	0.001		--
				--	KHSP1G	Thiacloprid (Low)	0.001		--
	<b>Herbicides (low level)</b>				KHSP92	Thiamethoxam (low)	0.001		--
KHSP59	2,4-D (low)	0.004		--	KHSP1H	Total Acetamiprid (Low)	0.003		--
KHSP60	2,4-DB (low)	0.004		--	KHSP94	Total Diuron (low)	0.0		--
KHSP49	3,4-Dichloroaniline (low)	0.001		--	KHSP82	Total Imazapic (low)	0.05		--
KHSP1J	Acetamiprid (Low)	0.001		--	KHSP90	Total Imidacloprid (low)	0.003		--
KHSP61	Acifluorfen (low)	0.004		--	KHSP69	Total Isoxaflutole (low)	0.004		--
KHSP43	Ametryn (low)	0.001		--	KHSP83	Triclopyr (low)	0.004		--
KHSP44	Atrazine (low)	0.001	13	--	KHSP84	Trifloxysulfuron (low)	0.004		--
KHSP45	Bromacil (low)	0.001		--					
KHSP62	Clomazone (low)	0.001		--					
KHSP91	Clothianidin (low)	0.001		--					
KHSP63	Cyanazine (low)	0.001		--					
KHSP46	Desethyl Atrazine (low)	0.001		--					
KHSP47	Desisopropyl Atrazine (low)	0.001		--					
KHSP48	Diuron (low)	0.001		--					
KHSP64	Ethametsulfuron methyl (low)	0.001		--					
KHSP50	Fluometuron (low)	0.001		--					
KHSP65	Fluroxypyr (low)	0.01		--					
KHSP66	Flusilazole (low)	0.001		--					
KHSP67	Haloxfop (acid) (low)	0.004		--					
KHSP51	Hexazinone (low)	0.001		--					
KHSP1C	Imazapic (Low)	0.001		--					
KHSP1D	Imazapyr (Low)	0.001		--					
KHSP68	Imazethapyr (low)	0.001		--					
KHSP52	Imidacloprid (low)	0.001		--					
KHSP89	Imidacloprid metabolites (low)	0.001		--					
KHSP70	MCPA (low)	0.004		--					
KHSP71	MCPB (low)	0.004		--					
KHSP72	Mecoprop (low)	0.004		--					
KHSP73	Mesosulfuron methyl (low)	0.001		--					
KHSP1I	Methoxyfenozide (Low)	0.001		--					



## Appendix B: Raw field and lab results (nutrients and major ions)

Table 8. Field measurements of physico-chemical parameters

Site	Date	Time	DO (mg/L)	EC (uS/cm)	pH	Temp (deg C)	Tur (NTU)
G8140312	8/10/2015	15:25	1.8	708	6.92	31.5	
G8140317	9/10/2015	09:15	1.5	728	6.91	31.6	
G8145358	8/10/2015	15:26	1.6	653	6.60	30.2	0.4
RN007821	21/10/2015	12:35	0.2	686	6.24	31.5	1.7
RN022397	22/10/2015	11:00	1.1	644	6.55	32.1	3.3
RN022486	6/10/2015	15:30	2.5	698	6.78	32.1	
RN022657	8/10/2015	10:00	1.5	621	6.46	29.7	0.1
RN023325	8/10/2015	11:25	0.1	665	6.50	30.7	0.1
RN023638	6/10/2015	09:00	5.7	717	7.02	30.2	
RN023648	8/10/2015	14:22	1.0	665	6.58	30.6	0.1
RN025126	20/10/2015	14:15	0.3	630	6.38	35.6	0.2
RN025636	7/10/2015	15:15	ns	903	6.35	30.2	0.4
RN026084	8/10/2015	14:26	3.5	643	6.10	31.7	
RN026142	7/10/2015	13:50	3.1	683	6.86	32.1	
RN026360	7/10/2015	16:40	3.9	656	6.29	31.8	0.1
RN029217	7/10/2015	15:15	2.4	731	6.84	31.2	
RN029953	6/10/2015	11:15	1.3	727	6.37	30.5	0.1
RN031066	6/10/2015	09:20	1.5	662	6.60	30.1	0.2
RN031332	7/10/2015	12:10	0.8	784	6.09	30.5	0.3
RN031879	8/10/2015	13:50	0.8	769	6.77	31.2	
RN032215	5/10/2015	15:15	1.5	715	7.04	28.9	0.2
RN032681	6/10/2015	16:40	0.8	735	6.42	30.1	0.4
RN033134	7/10/2015	11:00	4.5	678	6.83	33.3	
RN033291	8/10/2015	17:40	0.6	625	6.54	29.8	0.2
RN033343	8/10/2015	10:15	1.9	716	6.83	30.9	
RN034209	8/10/2015	08:50	6.1	605	6.91	33.1	
RN034903	7/10/2015	10:00	0.3	629	6.19	39.5	0.1

**Table 9. Nutrient concentrations**

Gcode	Date	Time	NH3_N (mg/L)	NO2_N (mg/L)	NO3_N (mg/L)	PO4_P (mg/L)	Total N (mg/L)	Total P (mg/L)
G8140312	8/10/2015	15:25	< 0.001	0.002	0.098	0.008	0.11	0.013
G8140317	9/10/2015	09:15	0.007	0.002	0.417	0.005	0.84	0.011
G8145358	8/10/2015	15:26	< 0.001	0.004	0.713	0.005	0.84	0.007
RN007821	21/10/2015	12:35	0.008	0.006	< 0.001	0.01	0.03	0.012
RN022397	22/10/2015	11:00	< 0.001	< 0.001	0.061	0.003	0.1	0.007
RN022486	6/10/2015	15:30	< 0.001	< 0.001	0.247	0.005	0.25	0.007
RN022657	8/10/2015	10:00	< 0.001	0.001	0.934	0.004	0.98	0.007
RN023325	8/10/2015	11:25	< 0.001	0.001	0.075	0.004	0.09	0.007
RN023638	6/10/2015	09:00	0.016	0.001	0.217	0.005	0.58	0.014
RN023648	8/10/2015	14:22	0.002	< 0.001	0.077	0.004	0.1	0.007
RN025126	20/10/2015	14:15	0.039	0.002	0.006	0.008	0.05	0.012
RN025636	7/10/2015	15:15	0.015	0.003	0.746	0.027	0.81	0.047
RN026084	8/10/2015	14:26	< 0.001	< 0.001	0.116	0.008	0.11	0.007
RN026142	7/10/2015	13:50	< 0.001	< 0.001	0.185	0.006	0.23	0.007
RN026360	7/10/2015	16:40	0.001	< 0.001	1.22	0.012	1.22	0.017
RN029217	7/10/2015	15:15	< 0.001	0.001	0.359	0.005	0.39	0.007
RN029953	6/10/2015	11:15	< 0.001	< 0.001	0.359	0.006	0.36	0.006
RN031066	6/10/2015	09:20	0.002	< 0.001	0.109	0.005	0.12	0.01
RN031332	7/10/2015	12:10	0.001	0.001	0.066	0.006	0.08	0.008
RN031879	8/10/2015	13:50	0.002	0.002	0.094	0.005	0.1	0.013
RN032215	5/10/2015	15:15	< 0.001	< 0.001	0.551	0.008	0.56	0.009
RN032681	6/10/2015	16:40	< 0.001	0.003	0.144	0.005	0.15	0.009
RN033134	7/10/2015	11:00	< 0.001	0.002	0.22	0.01	0.23	0.014
RN033291	8/10/2015	17:40	< 0.001	< 0.001	0.265	0.014	0.34	0.016
RN033343	8/10/2015	10:15	0.002	< 0.001	0.298	0.006	0.32	0.009
RN034209	8/10/2015	08:50	0.002	0.002	1.85	0.012	1.88	0.018
RN034903	7/10/2015	10:00	< 0.001	< 0.001	0.017	0.008	0.02	0.009

Table 10. Major cations and anions and general parameters

Site	Date	Time	Alka- linity	Ca_F (mg/L)	Cl (mg/L)	CO3 (mg/L)	EC lab (µS/cm)	Hard- ness (calc)	HCO3 (mg/L)	K_F (mg/L)	Mg_F (mg/L)	Na_F (mg/L)	OH (mg/L)	pH Lab	Si (mg/L)	SO4_F (mg/L)	TDS (mg/L)
G8140312	8/10/2015	15:25	380	86.5	5.6	< 1	652	383	380	3.2	40.5	6.0	< 1	8.2	15.3	< 5	380
G8140317	9/10/2015	09:15	377	82.0	12.3	< 1	696	378	377	4.1	42.0	13.1	< 1	8.3	12.4	10	400
G8145358	8/10/2015	15:26	362	82.9	10.4	< 1	651	363	362	2.6	38.0	8.5	< 1	8.3	9.7	< 5	360
RN007821	21/10/2015	12:35	366	106.0	3.0	1	679	407	366	2.2	34.8	3.5	< 1	8.1	12.0	< 5	410
RN022397	22/10/2015	11:00	328	85.2	5.1	1	513	368	328	3.1	37.7	5.5	< 1	8.2	13.0	< 5	360
RN022486	6/10/2015	15:30	371	95.3	4.5	< 1	631	387	371	1.4	36.1	3.5	< 1	8.3	9.7	< 5	380
RN022657	8/10/2015	10:00	334	84.0	8.6	< 1	570	345	334	2.0	32.9	7.0	< 1	8.2	8.6	< 5	350
RN023325	8/10/2015	11:25	370	100.0	6.1	< 1	631	381	370	1.4	31.8	4.7	< 1	8.2	9.9	< 5	370
RN023638	6/10/2015	09:00	482	97.9	5.6	< 1	641	394	482	1.7	36.4	4.3	< 1	7.8	10.7	< 5	380
RN023648	8/10/2015	14:22	379	87.0	5.4	3	656	385	376	3.0	40.6	6.1	< 1	8.4	13.5	< 5	390
RN025126	20/10/2015	14:15	277	80.0	6.7	1	518	335	277	4.8	32.8	7.4	< 1	8.3	13.9	26	360
RN025636	7/10/2015	15:15	299	61.1	19.7	11	594	341	288	2.6	45.7	13.6	< 1	8.5	17.4	< 5	380
RN026084	8/10/2015	14:26	329	91.4	3.8	< 1	557	346	329	1.3	28.6	3.4	< 1	8.3	9.1	< 5	340
RN026142	7/10/2015	13:50	348	81.7	8.0	3	637	364	344	2.8	38.7	7.3	< 1	8.4	9.3	< 5	370
RN026360	7/10/2015	16:40	348	81.8	12.9	< 1	623	360	348	1.2	37.8	8.4	< 1	8.3	15.8	< 5	380
RN029217	7/10/2015	15:15	381	92.8	6.3	< 1	579	387	381	1.6	37.7	7.8	< 1	8.2	14.2	< 5	400
RN029953	6/10/2015	11:15	407	93.6	6.5	< 1	608	408	407	1.3	42.3	6.1	< 1	8.2	14.6	< 5	410
RN031066	6/10/2015	09:20	365	85.7	5.3	< 1	573	375	365	3.0	39.1	6.1	< 1	8.2	15.0	< 5	380
RN031332	7/10/2015	12:10	455	127.0	4.0	< 1	771	470	455	1.3	37.2	5.0	< 1	7.7	14.7	< 5	460
RN031879	8/10/2015	13:50	398	106.0	12.3	< 1	663	420	398	1.6	37.7	9.7	< 1	8.0	13.1	< 5	410
RN032215	5/10/2015	15:15	362	83.0	19.5	< 1	652	374	362	3.1	40.4	16.9	< 1	8.3	13.2	< 5	400
RN032681	6/10/2015	16:40	411	105.0	7.5	< 1	669	427	411	1.5	39.8	6.2	< 1	8.2	13.7	< 5	430
RN033134	7/10/2015	11:00	341	90.4	13.6	3	584	364	338	1.8	33.7	8.2	< 1	8.4	13.3	< 5	390
RN033291	8/10/2015	17:40	342	103.0	6.3	< 1	558	359	342	1.5	24.5	6.4	< 1	8.2	9.5	< 5	330
RN033343	8/10/2015	10:15	369	91.6	5.8	2	599	390	367	1.3	39.1	5.9	< 1	8.3	15.0	< 5	390
RN034209	8/10/2015	08:50	269	75.2	16.4	9	360	303	260	0.9	28.0	11.5	< 1	8.5	16.6	< 5	320
RN034903	7/10/2015	10:00	315	71.4	7.8	4	543	331	311	4.8	37.1	8.2	< 1	8.4	15.9	10	350

## Appendix C: Herbicide and pesticide concentrations in Katherine region bores and springs.

**Table 11. Herbicide and pesticide concentrations in Katherine region bores.**

Only chemicals that were detected at a minimum of one site are shown. For a full list of analytes see Appendix A.

Site ID	NTG No.	2,4-Di- butylphenol	Atrazine	Desethyl Atrazine	Desisopropyl Atrazine	Haloxyfop (acid)	Imazapyr	Imidacloprid	Imidacloprid metabolites	Simazine	Tebuthiuron	Total Imidacloprid
DL Unit ANZECC*		0.1 µg/L NL	0.001 µg/L 13	0.001 µg/L NL	0.001 µg/L NL	0.004 µg/L NL	0.001 µg/L NL	0.001 µg/L NL	0.001 µg/L NL	0.001 µg/L 3.2	0.001 µg/L 2.2	0.003 µg/L NL
1	G8140312	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2	G8140317	ND	ND	<b>0.01</b>	<b>0.002</b>	ND	ND	ND	ND	ND	<b>0.002</b>	ND
3	G8145358	<b>1.3</b>	<b>0.004</b>	<b>0.032</b>	<b>0.011</b>	ND	ND	ND	ND	ND	ND	ND
4	RN007821	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
5	RN022397	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6	RN022486	ND	ND	ND	ND	ND	ND	ND	ND	ND	<b>0.002</b>	ND
7	RN022657	ND	<b>0.007</b>	<b>0.059</b>	<b>0.024</b>	ND	ND	ND	ND	ND	ND	ND
8	RN023325	ND	ND	<b>0.001</b>	ND	ND	ND	ND	ND	ND	ND	ND
9	RN023638	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
10	RN023648	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
11	RN025126	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
12	RN025636	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
13	RN026084	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
14	RN026142	ND	<b>0.002</b>	<b>0.004</b>	<b>0.002</b>	ND	ND	ND	ND	ND	ND	ND
15	RN026360	ND	ND	ND	ND	ND	ND	<b>0.16</b>	<b>0.008</b>	ND	ND	<b>0.17</b>
16	RN029217	ND	<b>0.003</b>	<b>0.006</b>	<b>0.003</b>	ND	<b>0.004</b>	ND	ND	ND	<b>0.001</b>	ND
17	RN029953	ND	ND	<b>0.002</b>	ND	ND	ND	ND	ND	<b>0.001</b>	ND	ND
18	RN031066	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
19	RN031332	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
20	RN031879	ND	<b>0.003</b>	<b>0.005</b>	<b>0.002</b>	ND	ND	ND	ND	ND	ND	ND
21	RN032215	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
22	RN032681	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
23	RN033134	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
24	RN033291	ND	ND	<b>0.002</b>	ND	ND	ND	ND	ND	ND	ND	ND
25	RN033343	ND	<b>0.001</b>	<b>0.005</b>	<b>0.002</b>	<b>0.001</b>	ND	ND	ND	<b>0.002</b>	ND	ND
26	RN034209	ND	ND	ND	ND	ND	ND	<b>0.77</b>	<b>0.028</b>	ND	ND	<b>0.8</b>
27	RN034903	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

\*guideline value from ANZECC and ARM CANZ (2000)

ND: not detected

NL: not listed

DL: detection limit

**Table 12. Locations and sampling dates for springs and bores in the Tindall Aquifer.**

<b>Bore ID</b>	<b>G Code</b>	<b>Date</b>	<b>Time</b>	<b>Latitude</b>	<b>Longitude</b>
1	G8140312	8/10/2015	3:25:00 PM	-14.4819354	132.2543538
2	G8140317	9/10/2015	9:15:00 AM	-14.4973429	132.2330155
3	G8145358	8/10/2015	3:26:00 PM	-14.4776689	132.2498067
4	RN007821	21/10/2015	12:35:00 PM	-14.5465318	132.3950326
5	RN022397	22/10/2015	11:00:00 AM	-14.4887364	132.2554468
6	RN022486	6/10/2015	3:30:00 PM	-14.4590542	132.2568027
7	RN022657	8/10/2015	10:00:00 AM	-14.4739935	132.2367814
8	RN023325	8/10/2015	11:25:00 AM	-14.4470505	132.2491836
9	RN023638	6/10/2015	9:00:00 AM	-14.4563031	132.2610076
10	RN023648	8/10/2015	2:22:00 PM	-14.4866829	132.2505494
11	RN025126	20/10/2015	2:15:00 PM	-14.5393742	132.1743558
12	RN025636	7/10/2015	3:15:00 PM	-14.4773272	132.4602574
13	RN026084	8/10/2015	2:26:00 PM	-14.3887664	132.1480462
14	RN026142	7/10/2015	1:50:00 PM	-14.4721654	132.2196282
15	RN026360	7/10/2015	4:40:00 PM	-14.5163438	132.4344973
16	RN029217	7/10/2015	3:15:00 PM	-14.4638842	132.2605439
17	RN029953	6/10/2015	11:15:00 AM	-14.4407431	132.2823309
18	RN031066	6/10/2015	9:20:00 AM	-14.4795477	132.2559946
19	RN031332	7/10/2015	12:10:00 PM	-14.4607183	132.3953667
20	RN031879	8/10/2015	1:50:00 PM	-14.3736376	132.1554372
21	RN032215	5/10/2015	3:15:00 PM	-14.6059757	132.4444998
22	RN032681	6/10/2015	4:40:00 PM	-14.4923259	132.330191
23	RN033134	7/10/2015	11:00:00 AM	-14.5786178	132.5076678
24	RN033291	8/10/2015	5:40:00 PM	-14.4284508	132.2082997
25	RN033343	8/10/2015	10:15:00 AM	-14.4622156	132.3108619
26	RN034209	8/10/2015	8:50:00 AM	-14.5395681	132.4675899
27	RN034903	7/10/2015	10:00:00 AM	-14.6184548	132.2018229