Surface Water Quality in the Upper Namoi

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Executive Summary

This project examined the quality of surface water and groundwater in the Quirindi-Gunnedah area of the Upper Namoi catchment in Australia's Murray-Darling Basin. While several studies have assessed salinity, this is the first project to examine a wide range of water quality parameters including nutrients and agricultural chemicals since the Liverpool Plains Water Quality project 1997/98. In addition, for the first time, many trace organic constituents related to human activity were assessed. Sampling was conducted in January 2012.

Surface water salinity was relatively low as expected (<1500 µS cm^{-1}, except Native Dog Gully), within Namoi CMA salinity targets. In contrast to most sample sites in the Mooki catchment, Native Dog Gully demonstrated salinity, sodium and chloride measurements that far exceeded all crop and drinking water salinity guidelines. However, this is partially mitigated by the negligible discharge, although this area remains a salinity hotspot. The surface water salt load calculated for 2011, 128600 tonnes/year, was slightly lower than that measured in 1998, 146000 tonnes/year. This negates predictions for an increase to 305,000 in 2020 (Beale *et al*. 1998).

However, groundwater salinity was found at levels above or approaching the upper limit of the Namoi CMA guideline for irrigation water, highlighting a gradual increase in groundwater salinity at some sites outlined by Timms *et al.* 2009.

Trace organics of anthropogenic origin were widely detected in both surface and groundwater, including pharmaceuticals, cosmetics and caffeine. Caffeine was the most widely detected organic and while most organics were not of concerning concentrations, their widespread presence raises questions as to the persistence of some human excretions in environmental waters. The only guideline exceeded was for atrazine and simazine with respect to the precautionary aquatic ecosystem protection guideline (99% of ecosystem inhabitants). However results did comply with crop and drinking guidelines.

The calculated hydraulic gradient from surface to groundwater values, suggests that rivers contribute a portion of the recharge to groundwater, although the magnitude of this remains undetermined. The stable isotope ratio of most groundwater samples was depleted relative to modern rainfall, suggesting primary recharge of those aquifers was from a wetter climate, or recharged during high intensity rainfall events, though the age of the water was not determined. Liquid Chromatography – Organic Carbon Detection (LC-OCD) a new technique for analysing dissolved organic carbon (DOC) in water, showed a clear differentiation between surface and groundwater. This is the first groundwater LC-OCD analysis in this area and presents scope for further study.

Contents

1 Background Information

This project examined the quality of surface water and groundwater in the Quirindi-Gunnedah area of the Upper Namoi catchment in Australia's Murray-Darling Basin. While several studies have assessed salinity, this is the first project to examine a wide range of water quality parameters including since the Liverpool Plains Water Quality project 1997/98. In addition, for the first time, many trace organic constituents related to human activity were assessed. Sampling was conducted in January 2012.

The Quirindi-Gunnedah area of the Upper Namoi catchment in Australia's Murray-Darling Basin is primarily dominated by irrigation and dryland cropping, with significant area also dedicated to irrigated pastures. The intensive usage of irrigation water, herbicide use and previous salinity concerns for this area represents water quality as a major concern. This is the first project since the Liverpool Plains Water Quality project 1997/98 to examine a wide range of water quality parameters, such as salinity, nutrients and agricultural chemicals. This also, for the first time, included analysis of trace organic constituents related to human activity. Of note, there are two proposed coal mining projects are within this area, Shenhua Watermark at Breeza and BHP Billiton project near Caroona.

The Namoi River, regulated with flow from Keepit Dam, is a subcatchment of the Murry Darling Basin drainage basin (Timms 1997). The unregulated Mooki River flows into the Namoi River at Gunnedah, starting at Pine Ridge and passing through Caroona and Breeza. Of the tributaries of the Mooki, it is noteworthy that Quipolly Creek is controlled with releases from Quipolly Dam, clearly distinguishable from the parallel stretch of the Quirindi Creek which often has no flow (Appendix 5, photo 1).

2 Aims and Objectives

The aims of this project were aligned with those of the Cotton Catchments Communities CRC.

- Examine the suitability of the Upper Namoi catchment surface water quality monitoring network,
- Examine past predictions of salinity increases in the Upper Namoi catchment,
- Contribute to the body of work on river health in the Upper Namoi, and
- Further understanding of surface-groundwater interactions.

3 Methodology

Sampling was conducted in January 2012; sample sites are outlined on the map in Appendix 1. Surface water samples were collected from the river surface using a 1L plastic beaker as close to the middle of the river as possible. The beaker was thoroughly rinsed out before each sample.

Unstable parameters (electrical conductivity, pH and temperature) were analysed immediately on site with a HACH water quality meter and calibrated sonde.

Samples for trace organics and LC-OCD analysis were collected in 1L and 300mL brown glass bottles, which were pre-cleaned and combusted to remove any attached carbon. Separate aliquots of 0.2 µm filtered water were taken for major anions and cations (acidified to 2% HNO_3), stable isotopes and alkalinity. All samples were stored at below 10 °C during transit and cooled in a refrigerator to 4°C overnight. All samples were analysed in the Analytical Centre at the University of New South Wales, except for alkalinity, which was analysed externally by ALS Group.

Groundwater samples were collected using a hand bailer, which was rinsed thoroughly at each location. Stagnant water is required to be purged from the casing of bores, and as such, only shallow bores were selected for sampling, where it was possibly to purge relatively low casing volumes with a hand bailer. However, two government bores, GW30086/1 and GW30081/1, and P20 at Cattle Lane have their results omitted in many analyses because they were not purged according to standard methods.

Surface water and piezometer elevations in metres Australian Height Datum (m AHD) were calculated from gauge stations or drillers log where available. However, the driller logs for older bores did not contain elevations and many surface water sites did not have gauges. In these cases, a topographic map and photographs were used to estimate the elevation. For the bores, once the elevation of the bore was found or estimated, the measured water level from the field was used to work out elevation of groundwater in m AHD (estimated height of bore casing was taken as 1m). The irrigation bores were not included in this data as the water level could not be measured.

The hydrographs presented in Figure 4.1.2 and 4.1.3 300m compared the water level at GW30000 to that of the Mooki River. However to compensate for the 300m distance from the bore to the River and the location of the river gauging station a further 2.5km upstream, a 5m elevation was applied to the groundwater level.

Salt load calculations were approximated from mean daily EC data and Daily discharge data, using the formula EC ($\mu S\ cm^{-1}$) * Discharge ($ML\ day^{-1}$) * 0.68 = Salt Load ($kg\ day^{-1}$) (Load Calculation Protocol, 2009).

Alkalinity samples were taken at nine of the twenty three sites and alkalinity at the remaining sites was calculated by difference from charge balance. The alkalinity results reported from the laboratory, were expressed as calcium carbonate, and converted to equivalent bicarbonate. This allowed charge balance errors (CBE) to be conducted with other ion data, by converting values in mg L^{-1} to meq L^{-1} and comparing the cation and anion sum in meq L^{-1}. Significant deviations from a CBE of zero indicates analytical inaccuracy, because water is of neutral charge. CBEs for the 9 samples with bicarbonate were all within 5%. The NO_3 data was found to be low enough to neglect in the ion balance calculations, reanalysis of this as N-NO_3 yielded similar low amounts.

4 Results and Discussion

4.1 Hydrology

To determine whether surface water is loosing or gaining to groundwater, the relative water levels of both must be compared. The approximate water heights at sample locations are represented in m AHD in Figure 4.1.1. The groundwater levels were generally lower than those of the river, the presence of a downwards hydraulic gradient indicates recharge from the river to groundwater. However, the quantity of recharge cannot be determined without knowledge of stream bed permeability. Hence it is not possible in this study to determine whether recharge from the river or recharge through the soil plain is the primary process of recharge.

Figure 4.1.1: Mooki catchment stream and ground water levels (m AHD; surface water and groundwater reading are coloured black and red, respectively)

A hydrograph from *Water Availability in the Namoi* (CSIRO 2007), Figure 4.1.2, shows the changing hydraulic gradient between the Mooki River and groundwater at Breeza. The fluctuating gradient implies both loosing and gaining conditions from the river. However, from 2002 onwards there is a sharp increase in the hydraulic gradient from the river to groundwater; implying increasingly losing conditions. These losing conditions were found to continue in 2011, shown in Figure 4.1.3, confirming the potential for river to groundwater recharge.

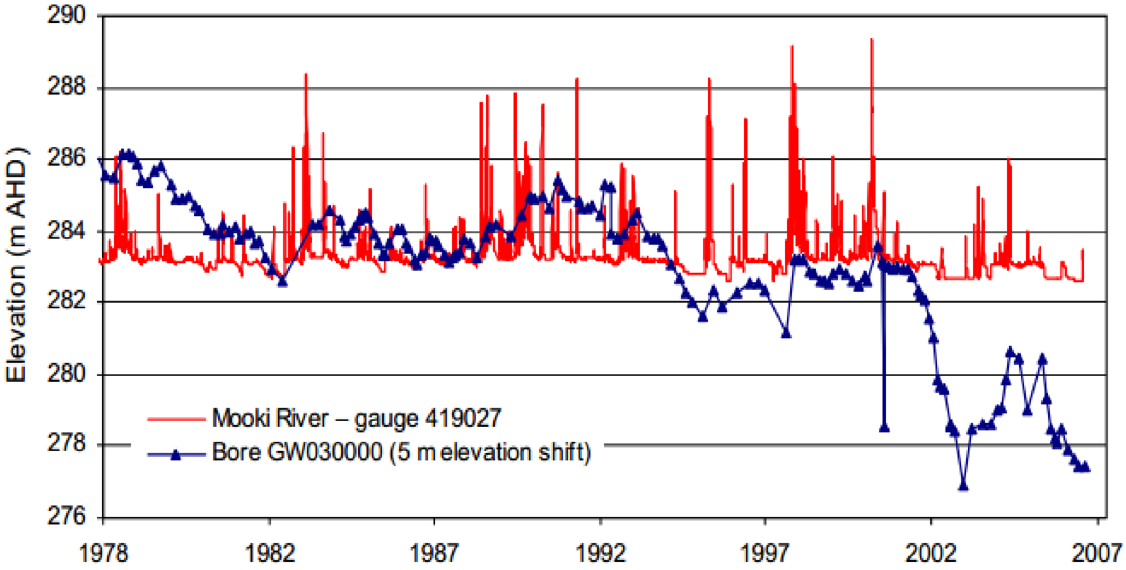

Figure 4.1.2: River and groundwater hydrographs at Breeza, showing loosing conditions from 1998 onwards. Source: CSIRO 2007

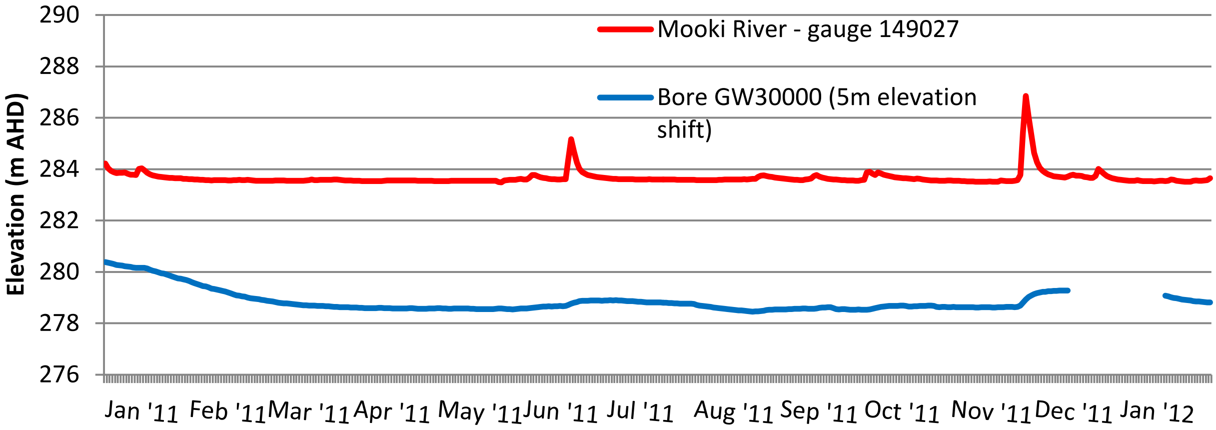

Figure 4.1.3: Comparison of groundwater to the Mooki River at Breeza, 2011, showing consistently loosing conditions. Screen depth for GW30000 was 254.4-271.1 m AHD.

High river flows in June and November evident in Figure 4.1.3 also shows a small, delayed response in the groundwater. Table 4.1.1 shows these two events in greater detail, confirming a small response to peak flows with a time lag.

Date of River peak	River increase (m)	Date of groundwater peak	Time delay for groundwater peak	Groundwater increase (m)	Rainfall (mm)*
18th June	1.561	4th July	17 days	0.138	9
28th November	3.304	11th December	15 days	0.637	115.6

Table 4.1.1: Comparison of peak river flow with peak groundwater level.

*Rainfall total for 4 days before river peak. Recorded at river gauging stations.

The stratigraphic log for GW30000 to the screening depth is displayed in Appendix 2. This shows the geology dominated by fine clay, with some silt, sand and fine gravel. The dominance of clay suggests a low permeability, though the approximate time of 16 days for a groundwater response suggests alternate flow pathways exist that are less clay dominated.

4.2 Salinity

Salinity data collected during peak flows in January are presented in Appendix 2 using electrical conductivity (µS cm^{-1}). This is visually summarised in Figure 4.2.1. The absolute human drinking water limit for salinity, 2500 µS cm^{-1} (Australian Drinking Water Guidelines 6 , 2011), was exceeded at Native Dog Gully (17460 µS cm^{-1}), P34 (4450 µS cm^{-1}) and P16 (42220 µS cm^{-1}) at the DPI Breeza research farm. These were also the only locations that the exceeded aquatic ecosystem guideline of 3000 µS/cm (ANZECC 2000). While the agriculture guidelines for salinity varies with different crops, the salinity category for tolerant crops and livestock, 5500 and 6250 µS cm^{-1}, was only exceeded at Native Dog Gully. However, the two aforementioned high groundwater values at the DPI Breeza research farm would result in a reduction in crop yield in tolerant plants and would be unsuitable for use with young plants and other intolerant crops (ANZECC 2000). All other samples recorded acceptable values.

The adjacent P34 and P16 bores on the Breeza research farm, west of Curlewis, had very high EC >4000 µS cm^{-1}, though P20 on the other side of the farm had a much lower EC of 1147 µS cm^{-1}. Similarly, two 15m deep windmill powered irrigation bores on a farm in the Breeza plain displayed a difference in EC of 728 µS cm^{-1}, despite only being 2.6km apart. This confirms the findings of Timms *et al*. (2009, figure 34) of the patchiness of salinity throughout the Namoi, with groundwater salinity increasing in areas near saline surface water and freshening in other areas with river leakage. While these shallow groundwaters are not extracted for use, they indicate the occurrence of more saline groundwater that could potentially flow into deeper fresh aquifers. The measured deep irrigation bores (30-60m) had an EC of 712-759 µS cm^{-1}, while the shallow windmill irrigation bores (15m) had an EC of 1201-1929 µS cm^{-1}. The latter exceeds the Namoi CMA salinity target for irrigation water of 650-1300 µS cm^{-1} (Namoi CMA 2007) and while this is generally appropriate for use with salt tolerant crops, it signals possible issues with the long term future of irrigation water in the Upper Namoi; echoing concerns of a steady increase in groundwater salinity at some sites reported by Timms *et al.* (2009, figure 66).

The Mooki River is a major tributary in the Namoi with inherently high salinity levels (Namoi CMA, 2007). From Figure 4.2.1 and the run-of-river quality graph, Figure 4.2.2, it is evident that the Mooki River displays a decline in EC downstream, consistent with previous observations from *Liverpool Plains – General Water Quality Report 1996/98*. A logarithmic scale is used in Figure 4.2.2 due the extremely high EC reading at Native Dog Gully, 17,460 µS cm^{-1}. The high outlier reading slightly downstream of Native Dog Gully suggests it this as a major source of salt into the Mooki.

Table 4.2.1 outlines a comparison between measured EC and continuous EC data from the only two EC gauging stations in the Upper Namoi. Considering the continuous data is a daily average of up to 130 samples the continuous EC measurements correspond closely enough with the field EC to confirm the accuracy these two continuous EC gauges.

Date: 25/1/2012	Instantaneous measured EC(μS cm^{-1})	Mean continuous EC(μS cm^{-1})	Percentage Difference (%)
Mooki River, Ruvigne	688	803	14
Namoi River, Gunnedah	264	228	14

Table 4.2.1: Comparison of measured EC to the daily mean recorded at each gauging station. Source: www.waterinfo.nsw.gov.au

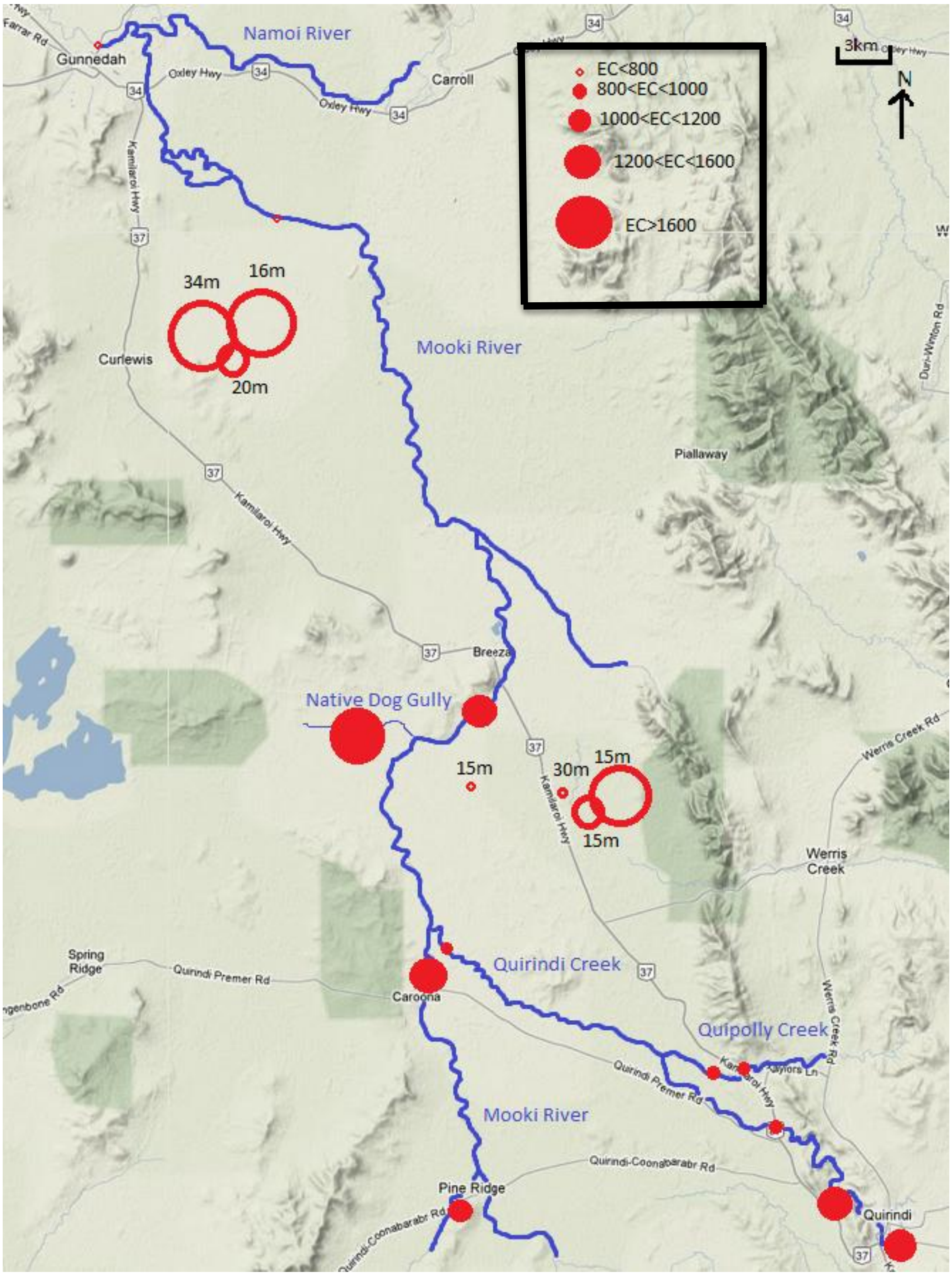

Figure 4.2.1: Distribution of EC values (μS cm^{-1}), grouped into 4 categories. Surface water and groundwater readings are represented by solid and open circles, respectively.

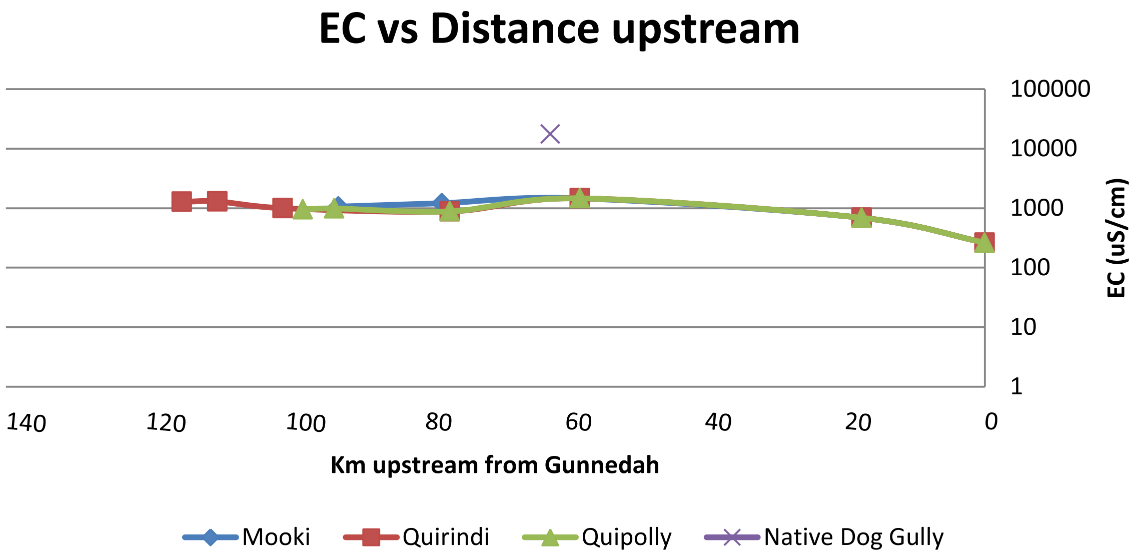

Figure 4.2.2: EC readings upstream from Gunnedah, plotted using a logarithmic scale (base 10). Distances were measured using the ruler in Google Earth.

Gunnedah iss a key site in the Namoi Catchment Management Authority (CMA) catchment action plan, with a river salinity target of 550 µS cm^{-1} 50% of the time and < 1000 µS cm^{-1} 80% of the time. The Gunnedah conductivity of 264 µS cm^{-1} satisfies this target; the similarity to the 1996/98 mean salinity of 306 µS cm^{-1} showing little change in the past 15 years (Liverpool Plains Water Quality Report, 1998).

The relationship between EC and stream height in the Namoi River at Gunnedah, Figure 4.2.3, shows a relatively small fluctuation in EC compared to larger fluctuations in stream height (due to water releases from Keepit dam), while that of the Mooki River at “Ruvigne”, Figure 4.2.4, shows a much higher fluctuation of EC with a smaller change in stream height (the Mooki is unregulated). Both graphs form a moderate inverse relationship with a correlation co-efficient of -0.413 and -0.454(Pearson method) for Ruvigne and Gunnedah respectively. This confirms the Mooki with high inherent salinity and signals low discharge allowing salt to accumulate, with flood events flushing out the high salinity water. This demonstrates the greater concern salinity poses under flood conditions.

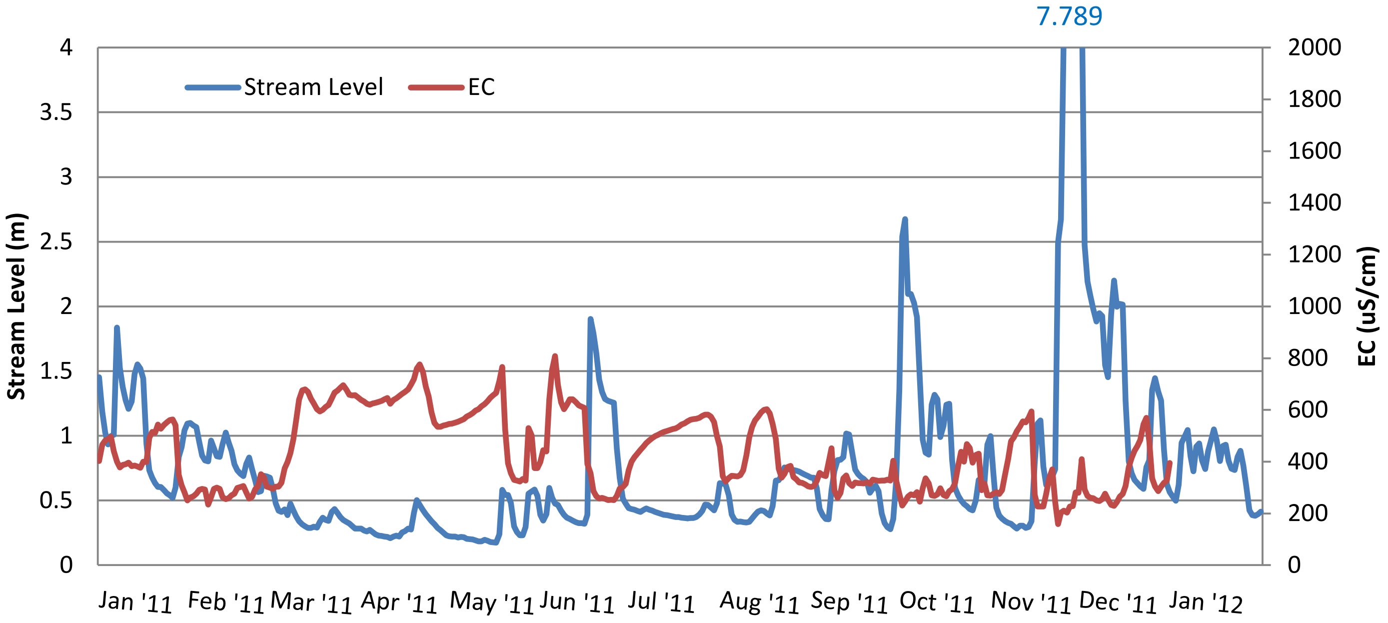

Figure 4.2.3: Stream level with Electrical Conductivity in the Namoi River at Gunnedah. Peak of 7.789m in Nov ’11 omitted to preserve graph readability. Correlation Co-efficient= -0.454

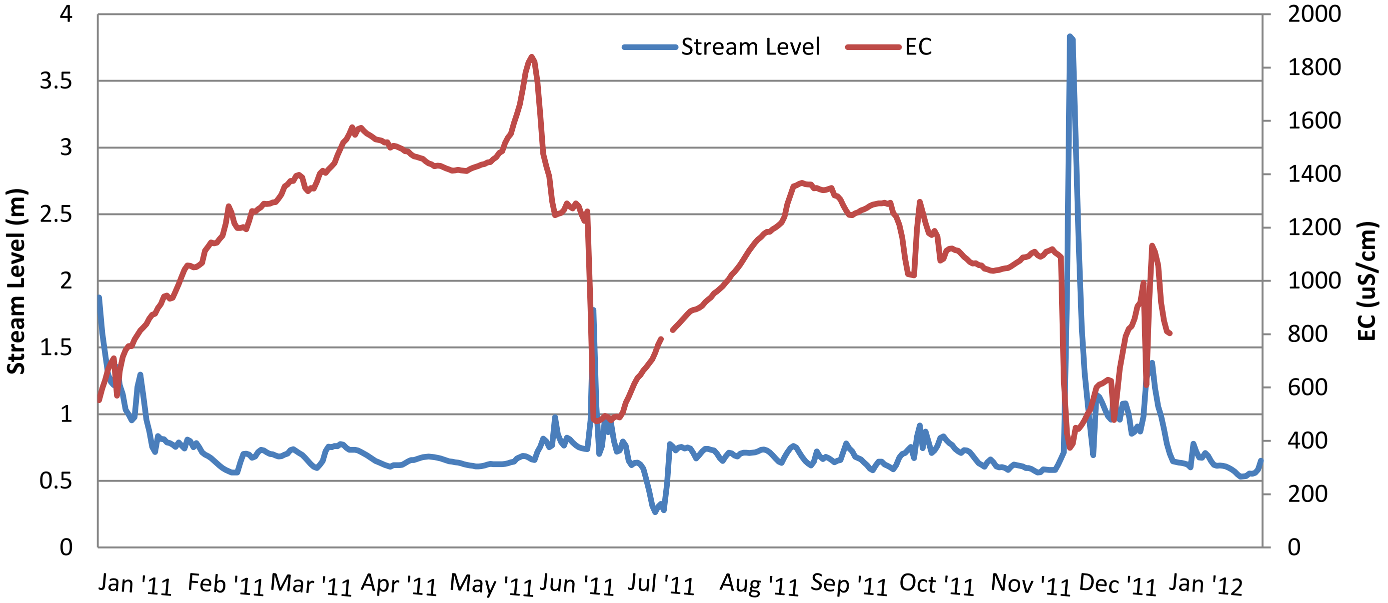

Figure 4.2.4: Stream level with Electrical Conductivity in the Mooki River at ‘Ruvigne’. Correlation co-efficient= 0.413

While EC readings are one way to assess salinity issues, it does not take into account the quantity of salts being transported by the river or the salt load. Salt loads for the Namoi at Gunnedah and Mooki at Ruvigne are presented in Figure 4.2.5. This clearly shows a much greater salt load in the Namoi, with the Mooki only exhibiting comparable loads to the Namoi in flood events.

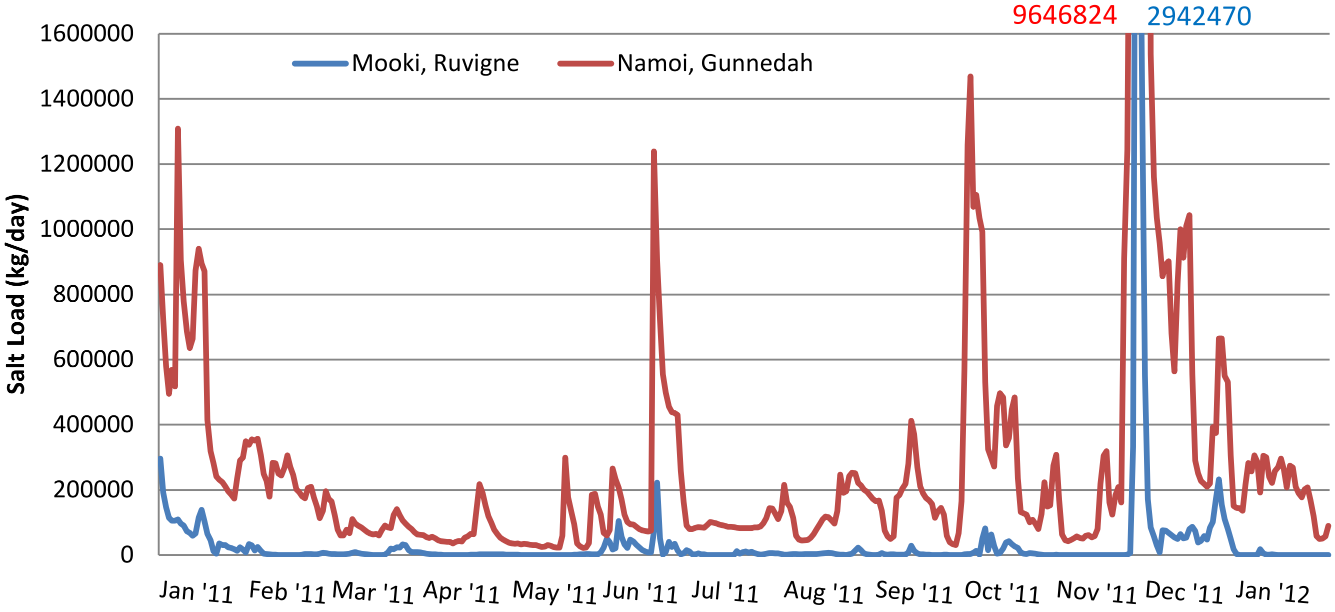

Figure 4.2.5: Daily salt load at Ruvigne and Gunnedah. Peak of 9,64,684kg/day and 2,942,470kg/day for the Namoi and Mooki respectively are omitted to preserve graph readability

The yearly salt load was calculated as the area under the graph for 2011. This is summarised in table 4.2.2 and shows the Namoi with over eight times the annual salt load of the Mooki. This is in complete contrast to the high measured EC in the Mooki and low measurement in the Namoi. Table 4.2.2 also shows the 2011 Namoi salt loads slightly lower than those measured in the Namoi in 1998 and much less than the prediction for 2020 (Beale *et al*. 2000). This data shows that salt quantities as not such as significant as predicted. However, the last ten years of drought should be taken into consideration and future wetter years could result in a large increase in salt loads.

All values in tonnes/year	Mooki '11	Namoi '11	Namoi Measured '98	Namoi Predicted '20
Yearly Salt Load	14,700	128,600	135,600	305,000

Table 4.2.2: Comparison of yearly salt loads. Source: Beale *et al*. 2000

4.3 Major Ions

The major ion results of are summarised in Appendix 2. All sodium and chloride guidelines, outlined in Table 4.3.1, were greatly exceeded by samples at Native Dog Gully (Na: 2788mg/L, Cl:6208 mg/L) and P20 at Cattle Lane (Na:1655mg/L, Cl:3482mg/L) and GW30081/1 off Quirindi Creek (Na: 513mg/L, Cl:1557mg/L). While these were not used as irrigation water, the degree to which the guidelines were exceeded represents a major concern if these waters ever leak into irrigation water. The only other guideline exceeded was the sodium drinking water quality guideline at the shallow irrigation bore (Sample #19, Na:368mg/L). While this guideline only upholds the 'aesthetics' of drinking water and is not based on health concerns, the very large sodium percentage at this bore, seen as the outlier 'farmer bore' in the cation ternary graph in Figure 4.3.2, reinforces concern for the potential for irrigation water to exceed sodium crop guidelines.

Values in mg/L	Sodium drinking water guidelines[1]	Chloride drinking water guideline[1]	Sodium 'tolerant' crop guideline[2]	Chloride 'tolerant' crop guideline[2]
Concentration	180	250	460	700

Table: 4.3.1: Comparison of sodium and chloride guidelines

[1] Australian Drinking Water Guidelines 6, 2011. No health-based guidelines, values based purely on aesthetic value.

[2] ANZECC 2000. Guidelines to prevent foliar injury.

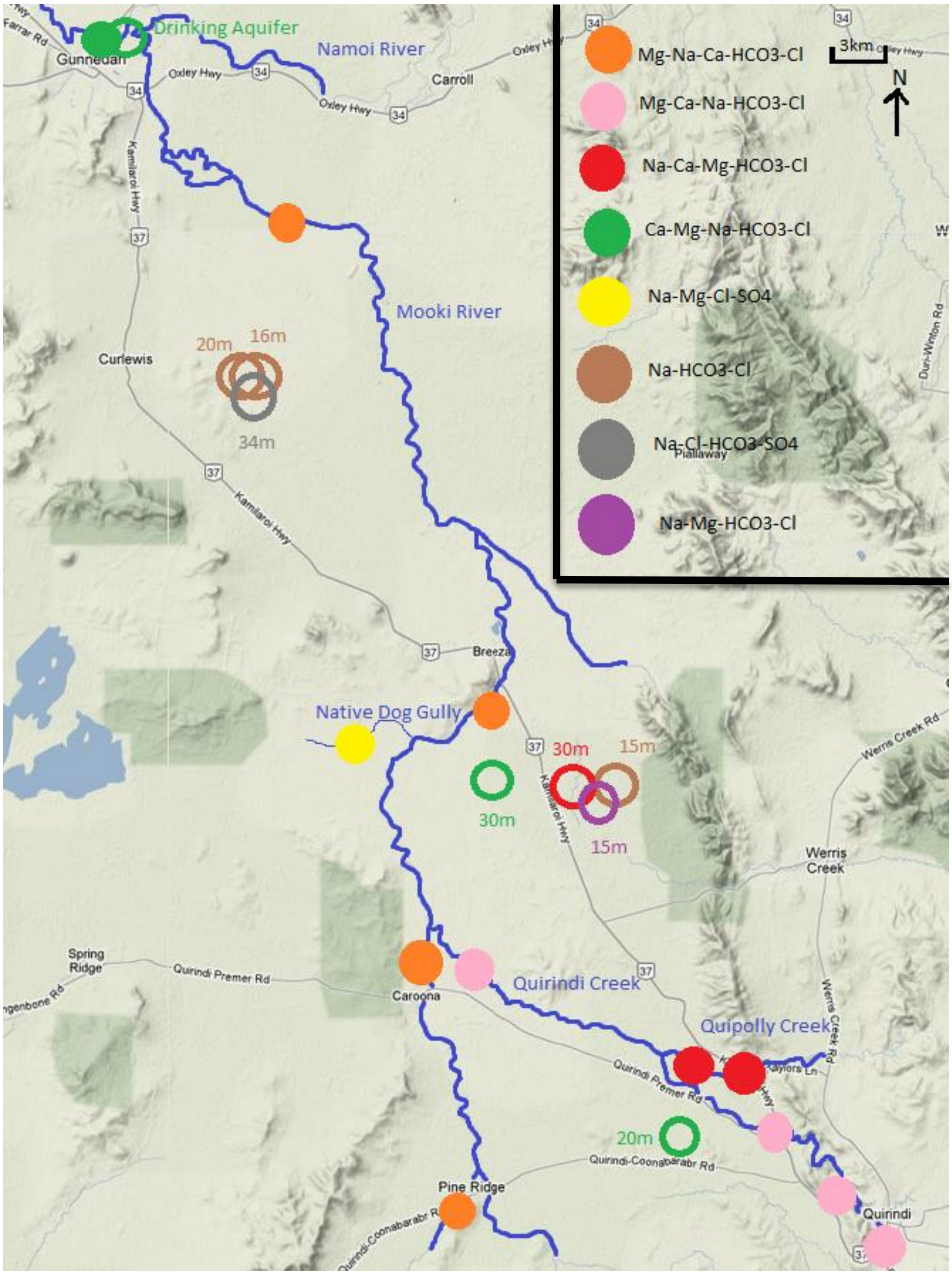

Figure 4.3.1: Distribution of different water types. Surface water and groundwater readings are represented by solid and open circles, respectively.

The major ion data was used in Aquachem® to calculate the water type. This is visually displayed in Figure 4.3.1; the distinctive water types allowed relative flow to be determined. The Mg-Na rich water from the upper Mooki dominates the Mg-Ca rich water from the adjoining Quirindi Creek and the Na-Mg water from Native Dog Gully. However, the flow of the Mooki into the Namoi is relatively low, seen by the distinct Ca-Mg water type in the Namoi at Gunnedah.

The major ion data was also prepared into a piper diagram using Aquachem®, Figure 4.3.2. A piper diagram contains separate ternary plot of cations and anions which are then matrix transformed into a diamond displaying both sets of data. The Mooki, Quirindi and Quipolly river samples were well grouped, the similar water composition suggesting significant mixing between them. However, the Namoi River and Native Dog Gully showed a significantly distinct water composition, implying only a small interaction between the rivers. The similarity of the Namoi River sample at Gunnedah with the Gunnedah drinking water suggests recharge of the deep aquifer from the river. The deep farmer bores (30-60m) were of similar water type to the Mooki River, whilst the two shallow (windmill, 15m) irrigation bores were quite distinct indicating different processes involved.

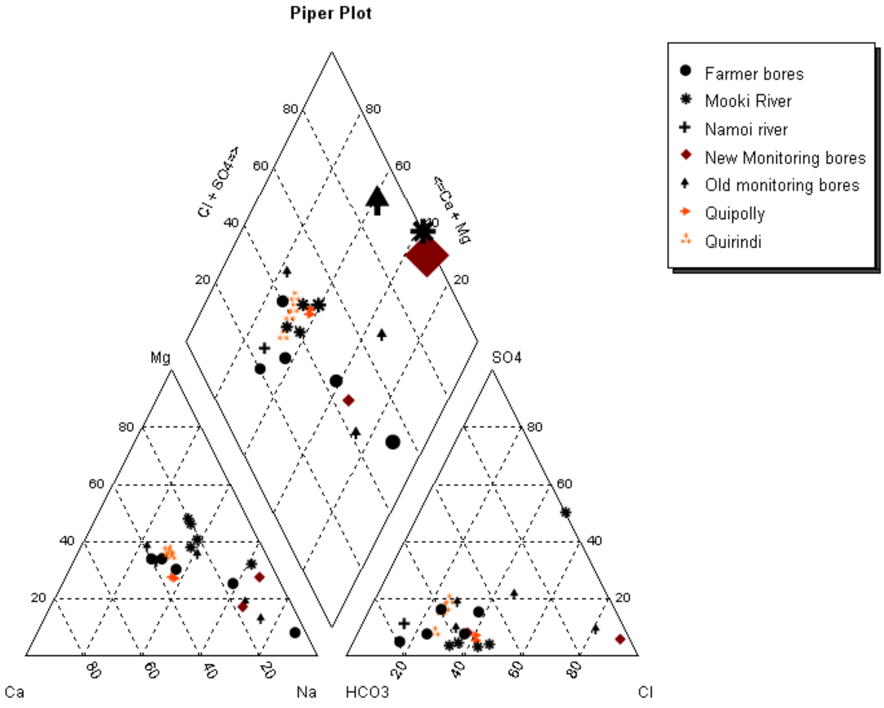

Figure 4.3.2: Piper diagram showing ion composition of sampled water from January 2012

The piper diagram from Timms *et al.* 2002, Figure 4.3.3, shows the change in composition of shallow groundwater due to drainage of irrigation water from deep aquifers. Figure 4.3.3 shows a similar composition to that in Figure 4.3.2, and includes three of the same sites at Breeza research farm.

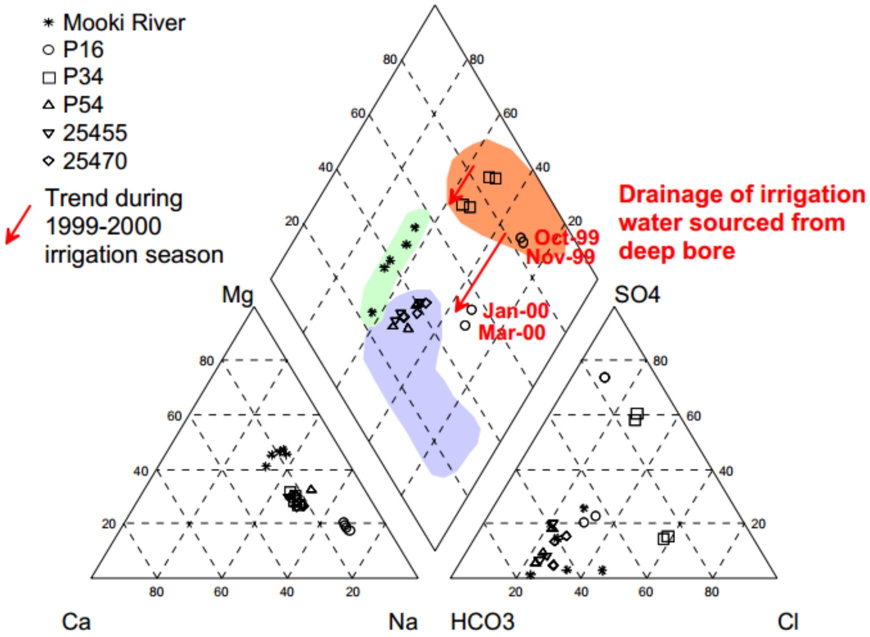

Figure 4.3.3: Piper diagram showing the impact of deep groundwater used as irrigation on shallow aquifers. Source: Timms *et al.* 2002

4.4 Trace Organics

A summary of the trace organics detected in Oct 2011 and Jan 2012 is presented in Appendix 4. Most detections were less than 50ng L^{-1}. It is of note that the unit ng L^{-1} is equivalent to parts per trillion, ie. 1 ng L^{-1} of a trace organic is equivalent to one molecule per trillion other molecules.

Many of these are rapidly photo or bacterially degraded, suggesting a local contamination source. However, the conservative (non-reactive) organics were also detected, often with a higher frequency and concentration, indicating that both local and upstream sources of contamination were present. Many of the chemicals detected were of an anthropogenic origin, primarily pharmaceuticals but also included cosmetics, toothpaste and caffeine; most samples did not exceed concentrations of 20ng/L. The uncommon nature of many of these chemicals in waterways is reflected in the absence of water quality guidelines for most of them. Nonetheless, it is unlikely these chemicals will ecologically or agriculturally have any impact at such low concentrations. They do however play and important role as tracers, raising concerns regarding the persistence of human waste throughout the waterways of the Upper Namoi.

One proposed source of contamination was sewage treatment plant in Quirindi (Appendix 5, photo 2), though samples upstream and downstream did not indicate that to be a source of human waste.

Caffeine was the most widespread of the trace organics, present in 23/34 samples with a maximum concentration of 274ng/L. Graphs to correlate detection and concentration of caffeine and other anthropogenic trace organics were inconclusive.

The detection of the trace organics in groundwater was unexpected. Considering the installation of the bore as a source of contamination, P20 at DPI Breeza research farm, installed in April 2010, was compared to the other groundwater samples from bores that were installed more than ten years ago. While P20 proved to have a higher frequency and much higher concentration of trace organics than any other bore, but t-octylphenol, polyparaben, paracetamol, caffeine, TCEP, Enalpril, Risperidone, Atrazine and DEET were still found in traces in the older bores. This implies the installation of the bore is only a contributing factor to the organics in the groundwater.

It is worth highlighting one of the deep irrigation bores (Sample No. 18) from the research farm on the Breeza Plain displayed an unusual caffeine reading of 192ng L^{-1} and a high polyparaben (ingredient of cosmetics) concentration of 1600ng L^{-1}. However, the absence of the same chemicals another groundwater bore(Sample No. 19) 1.3km away, which draws from the same aquifers, suggest a source of contamination to be local rather than widespread in the deep aquifers (30-60m).

The only guideline exceeded was the ANZECC Aquatic Ecosystem guideline, by the two herbicides, Atrazine (4/22) and Simazine (1/22). However, taking into account the limited number of samples exceeding the guidelines and the use of the precautionary figure to protect 99% of ecosystem inhabitants, the results are not of a major concern. If the 95% values of 13,000 ng L^{-1} and 3,200 ng L^{-1} for Atrazine and Simazine respectively were used, the guidelines would not have been exceeded at all. Notably, the concentrations were acceptable with regard to drinking water guidelines.

Measurements in µg L^{-1}	Oct '11	Jan '12	Total '11/'12	Total '96/'97
Range of Atrazine detections	0.007-0.763	0.005-5	0.005-5	0.04-14
Mean	0.182	0.951	0.567	0.42
Median	0.077	0.047	0.062	0.02
Frequency of atrazine detections	9/11	16/19	25/30	34/84
Percentage	82	84	83	40.5

Table 4.4.1: Comparison of Atrazine detections from '11/'12 with '96/'97 (Timms *et al.* 1997)

Table 4.4.1 compares the detections of Atrazine with those detected in the *Liverpool Plains Water Quality Project*. While the mean and median values are similar, there is a significant difference in frequency of detections. However, this can be attributed to the improvement in detection limits of Atrazine from 100ng L^{-1} in 1997 to 5ng L^{-1} in 2011. Factoring the different detection limits and the different sample locations, Atrazine extent and concentration has changed little since 1997.
The distribution of atrazine concentrations is mapped in Figure 4.4.1. This shows significant Atrazine detection limited to the Mooki River, though the varying concentrations along the river suggests the high concentrations are due to various point sources; most likely due to run-off from farm sprayings. Notably, groundwater was only found to contain traces of Atrazine.

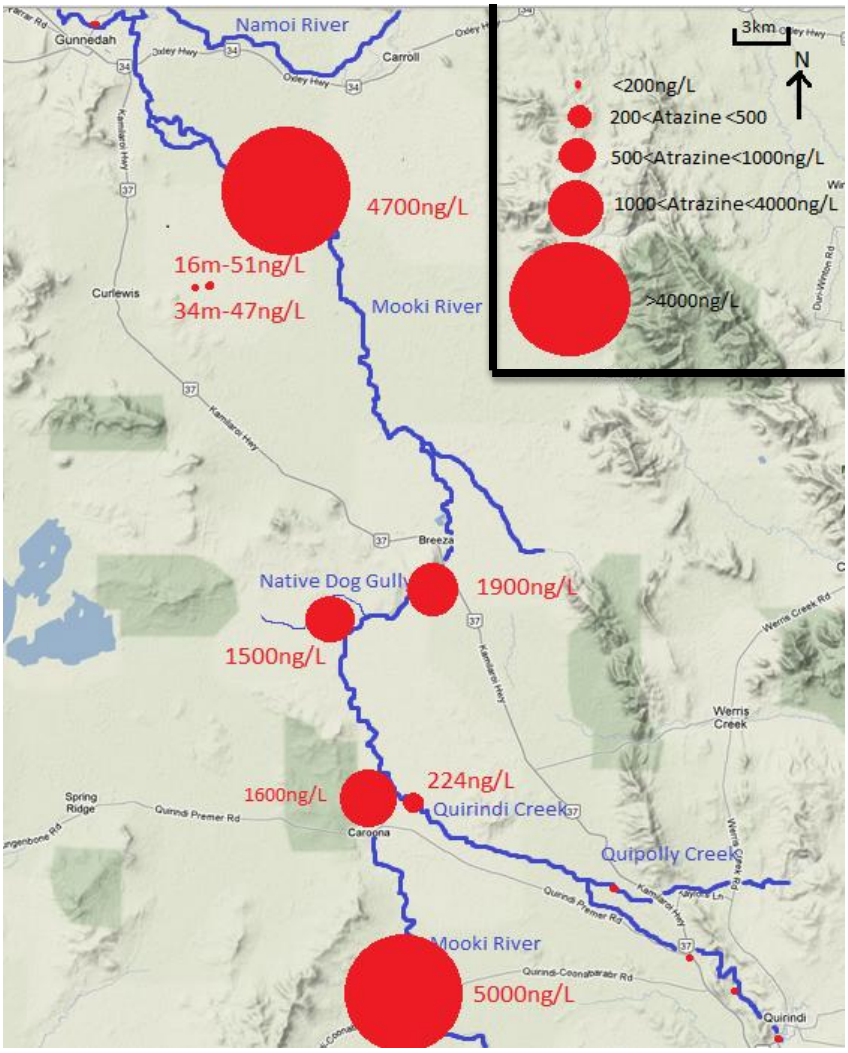

Figure 4.4.1: Distribution of Atrazine throughout sampled locations in the Upper Namoi

4.5 Stable Isotopes

The preferential evaporation of lighter isotopes in water allows the isotopic signature of stable, heavier isotopes deuterium (δ^{2}H) and oxygen-18 (δ^{18}O) to determine relative quantities of evaporation and conditions of rainfall input.

The stable isotope ratios are plotted in Figure 4.5.1 with the Local Meteroic Water Line (LMWL) for Gunnedah, $\delta^{2}H = 8.41\ \delta^{18}O + 15.99$, the Global Meteoric Water Line (GMWL), $\delta^{2}H = 8.13\ \delta^{18}O + 10.8$ and Gunnedah rainfall average of $\delta^{18}O = -4.86‰$ and $\delta^{2}H = -24.67‰$ (Andersen *et al.* 2008).

All deep groundwater bores (>25m) and some shallow groundwater bores were in line with the GMWL, consistent with isotope values for deep groundwater in Timms *et al*. (2002). These were clustered in the region with depleted δ^{2}H and δ^{18}O isotope ratios relative to modern rainfall. This indicates recharge of this groundwater occurred a while ago under wetter or more intense rainfall events, though the exact age cannot be determined from this data (Lavitt 1999).

The shallow groundwater samples with very similar isotope ratios to modern rainfall, Cattle Lane P20 and GW30086/1, suggest significant recharge directly from rainwater. This is in line with observations of a very high water level at P20 at Cattle Lane (2m below marker) and the positioning of GW30086/1 alongside the dry stretch of Quirindi Creek (Appendix 5, Photo 1), which indicates fast pathways for recharge at both locations. The only groundwater sample to display enriched isotope ratios was at P16 located on the DPI Breeza research farm.

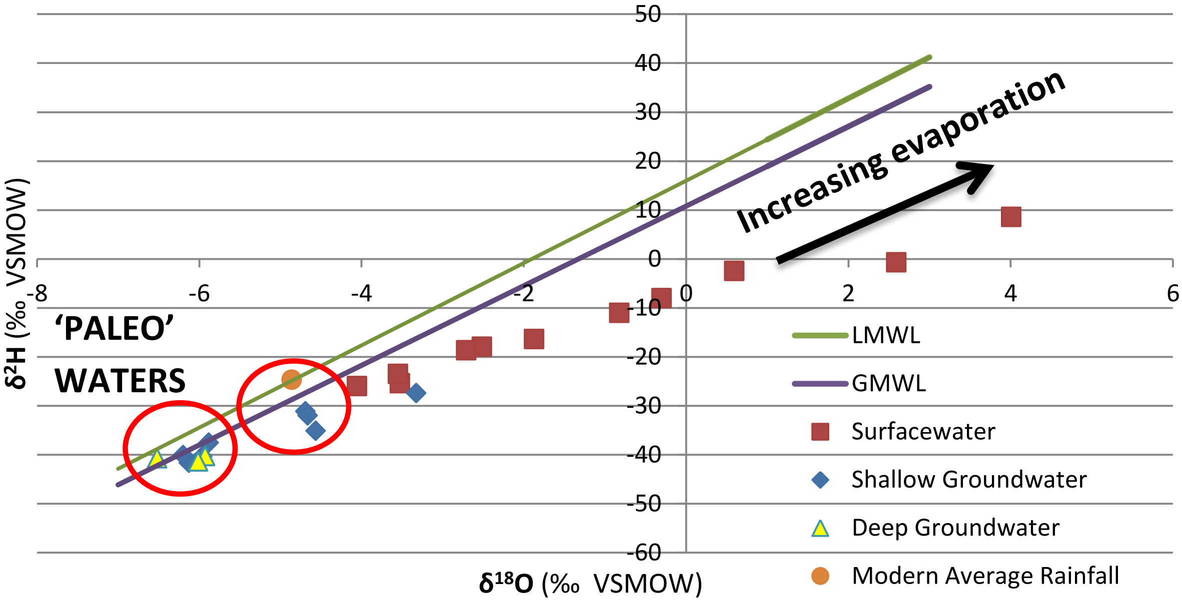

Figure 4.5.1: Stable Isotope ratios for Jan '12 compared with the GMWL, LMWL and Modern Average Rainfall (Andersen *et al.* 2008)

The spread of the surfacewater samples shows a clear trendline of enriched isotope ratios relative to modern rainfall. This shows a variation in evaporation, with heavier isotopes less likely to evaporate. This suggests the two outlier samples with the highest enrichment, Native Dog Gully and Quirindi Creek at Caroona, have more stagnant water and low flow. This shows the limited impact these two creeks have in contributing to the Mooki.

The stable isotopes in October 2011, Figure 4.5.2, displayed very similar data to January 2012, with the range of values closely corresponding. The greater spread of groundwater samples in October 2011 could be attributed to the wider range of groundwater depths which samples were obtained from.

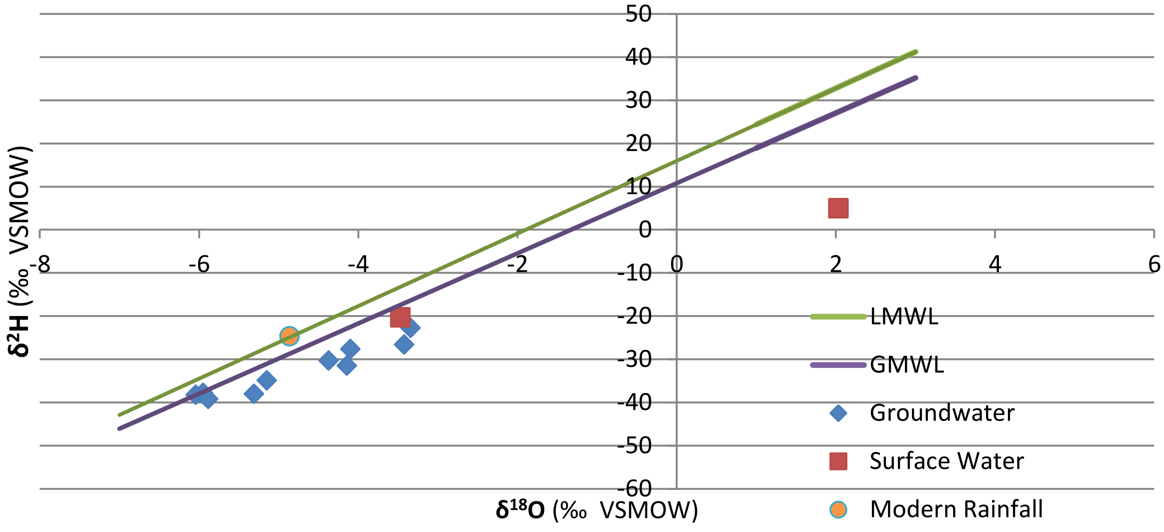

Figure 4.5.2: Stable isotope ratios for Oct '11 compared with the GMWL, LMWL and Modern Average Rainfall (Andersen *et al.* 2008)

4.6 Humic Substances

The Humic Substances diagram (HS-diagram), Figure 4.6.1, represents the composition of separated organic carbon constituents in water. This diagram is derived from analysis using Liquid Chromatography – Organic Carbon Detection (LC-OCD), which fractionates organic matter into different classes of compounds for detection. Additional analyses such as UV-absorbance are also conducted, allowing the comparison with standards to produce the HS-diagram (Huber, 2005).

Figure 4.6.1 shows a clear distinction between surface and groundwater. This is highly significant as LC-OCD is a relatively new technique and as of the author's knowledge, no LC-OCD analysis of groundwater has yet been published and presents significant scope for future research.

The surface water dissolved organic matter (DOM) was strongly aligned to the pedogenic-aquagenic line, indicating a gradient from pedogenic to aquagenic. Aquagenic carbon is generated by excretion and decomposition of aquatic bacteria and plankton. This generally is composed of high molecular weight carbohydrates and proteins which are relatively labile (de Lacerda 2004, pg204; Lawler 2004, pg 7). The outlier surface water sample was at Native Dog Gully, the lower aromacity and molecularity, suggests the water has been significantly processed. This confirms the observation in the stable isotope ratios, indicating stagnant water.

Groundwater samples were 'well mineralised', as groundwater DOM displayed lower aromacity and molecularity than the surface water DOM. This indicates the samples had undergone substantial microbial breakdown.

The categorisation of groundwater into different depth piezometers (shallow <25m, Deep >25m) and irrigation bores did not yield any determinable trends.

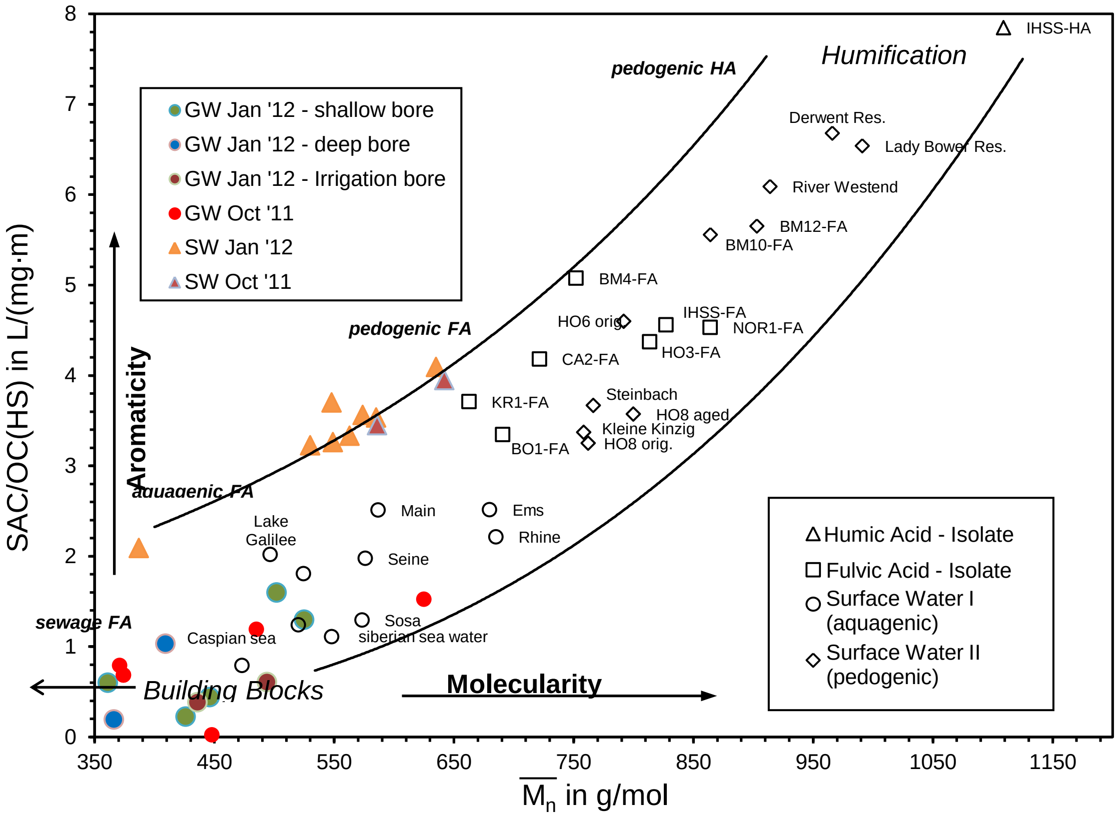

Figure 4.6.1: H-S Diagram showing a clear distinction in groundwater and surface water DOM. (SW= Surface Water, GW= groundwater)

5 Conclusions

Evidence suggests water quality in the Upper Namoi complies with most water quality guidelines. There was no significant change in water detected since the Liverpool Plains Water Quality project (1996/97) for the sites included in this project

Most sites demonstrated acceptable salinity, with low EC readings in the Namoi River at Gunnedah falling well below Namoi CMA targets and the Mooki River demonstrating EC levels typical of its high inherent salinity. Salt loads showed a much higher salt quantity in the Namoi River than the Mooki, indicating this is of more concern than the salinity in the Mooki. Yearly salt load in the Namoi River at Gunnedah in 2011 (128,600 tonnes/year) was slightly lower than that measured in 1998 (135,600 tonnes/year), in contrast to predictions of a sharp increase to 305,000 tonnes/year in 2020. While this shows salinity is not as concerning an issue as predicted, it should be noted that this result is after ten years of drought and considerably increased rainfall may result in this issue arising again.

Continuous EC gauging stations at 'Ruvigne' and Gunnedah were compared to EC field measurements, with results close enough to confirm their accuracy. However, the existence of only two working EC gauges in the Upper Namoi may compromise effective observations of salinity across the Upper Namoi.

Samples at the DPI Breeza research farm bores, P16 and P34, were the only groundwater samples to exceed crop and drinking water salinity guidelines. While these shallow groundwaters are not extracted for use, they indicate the occurrence of more saline groundwater that could potentially flow into deeper fresh aquifers. Most bores were of acceptable salinity, falling within the Namoi CMA target range of 650-1300 µS cm^{-1} for irrigation water, however, a few exceptions highlight concern for gradually increasing groundwater salinity raised in Timms *et al*. 2009.

Sodium and chloride concentrations pose a potential concern with three isolated samples vastly exceeding and one shallow irrigation bore found to approach the ANZECC 2000 primary industry guidlines. The very high concentrations represent a potential concern if mixing of this very high sodium and chloride concentration water into irrigation aquifers occurs.

Native Dog Gully demonstrated the highest EC of 17460 µS cm^{-1}, exceeding all crop water quality guidelines. Native Dog Gully also contained sodium and chloride concentrations far exceeding guidelines to prevent foliar injury to crops and had atrazine concentrations exceeding ecosystem protection guidelines. However, this is partially mitigated by almost non-existent flow out of Native Dog Gully, which is observable in its unique water composition shown in the piper diagram, highly enriched stable isotope ratio and processed DOM position on the HS-diagram.

Trace organics of anthropogenic origin, including pharmaceuticals, cosmetics and caffeine, were widely detected in the Upper Namoi. While most organics were not of concerning concentrations, their widespread presence raises questions as to the persistence of some human excretions in environmental waters. Caffeine was the most widely detected trace organic, even widely detected in groundwater. The higher frequency and concentration of organics found at a piezometer installed in 2010 (P20 Breeza research farm) compared to older piezometers (all >10 years old) indicates contamination during bore installation is a contributing factor to trace organics in groundwater. The only guideline exceeded was the highly precautionary aquatic ecosystem protection guideline (99% of ecosystem inhabitants) by atrazine and simazine. However, the adherence to crop and drinking guidelines and low frequency of detection indicates these results are not of a major concern. The distribution and concentration of atrazine detections showed no significant changes from those detected in the *Liverpool Plains Water Quality Project 1997* for the limited number of sites included in this project. The lack of improvement is surprising, given improved BMP (best management practices) for chemical applications, handling, disposal and recycling of chemical containers.

River based groundwater recharge was indicated by the presence of a hydraulic gradient from river to groundwater. Observations of peak river flow events in the Breeza hydrograph shows a small delayed response in groundwater, taking on average 16 days to reach a reduced groundwater peak. However, it was not possible to determine the quantity of recharge or whether it is the primary means of recharge.

Stable Isotope data water from all deep and some shallow aquifers were found to be depleted relative to modern rainfall measured in Gunnedah; suggesting recharge was primarily from a paleoclimate with wetter or higher rainfall conditions. However, the age of water cannot be determined as radioisotopes were not analysed.

LC-OCD analysis showed a clear difference between ground and surface water and further study should be undertaken to understand the processes contributing to these distinctive results.

6 Recommendations

- Further research on the occurrence of trace organics; origin, transport, fate and degradation pathways, particularly those organics of human origin. These trace organics may also provide useful tracers of seepage and recharge.
- Installation of automated continuous level monitoring in bores at various depths directly adjacent to river gauging stations to further understanding of river-based recharge.
- Continue to monitor salinity and salt loads, particularly after large flood events. The condition of the EC monitoring network near salinity hotspots and along the upper Namoi River is important.
- Monitor groundwater near Native Dog Gully to determine whether it has any impact of surrounding aquifers.
- Sampling and analysis of radio-isotopes to determine the residence time of groundwater, and any recent changes in recharge sources.
- Further in-depth research with LC-OCD analysis of surface and groundwater seeking to understand the processes contributing to the distinctive results.

7 Presentations and Public Relations

Presentations and public relations are a very important part of research programs at UNSW. The findings of this research project will be made available through a web article, a poster, contributions to local newspapers (through the upcoming water series) and will be included in future workshop and open day presentations in the Namoi catchment.

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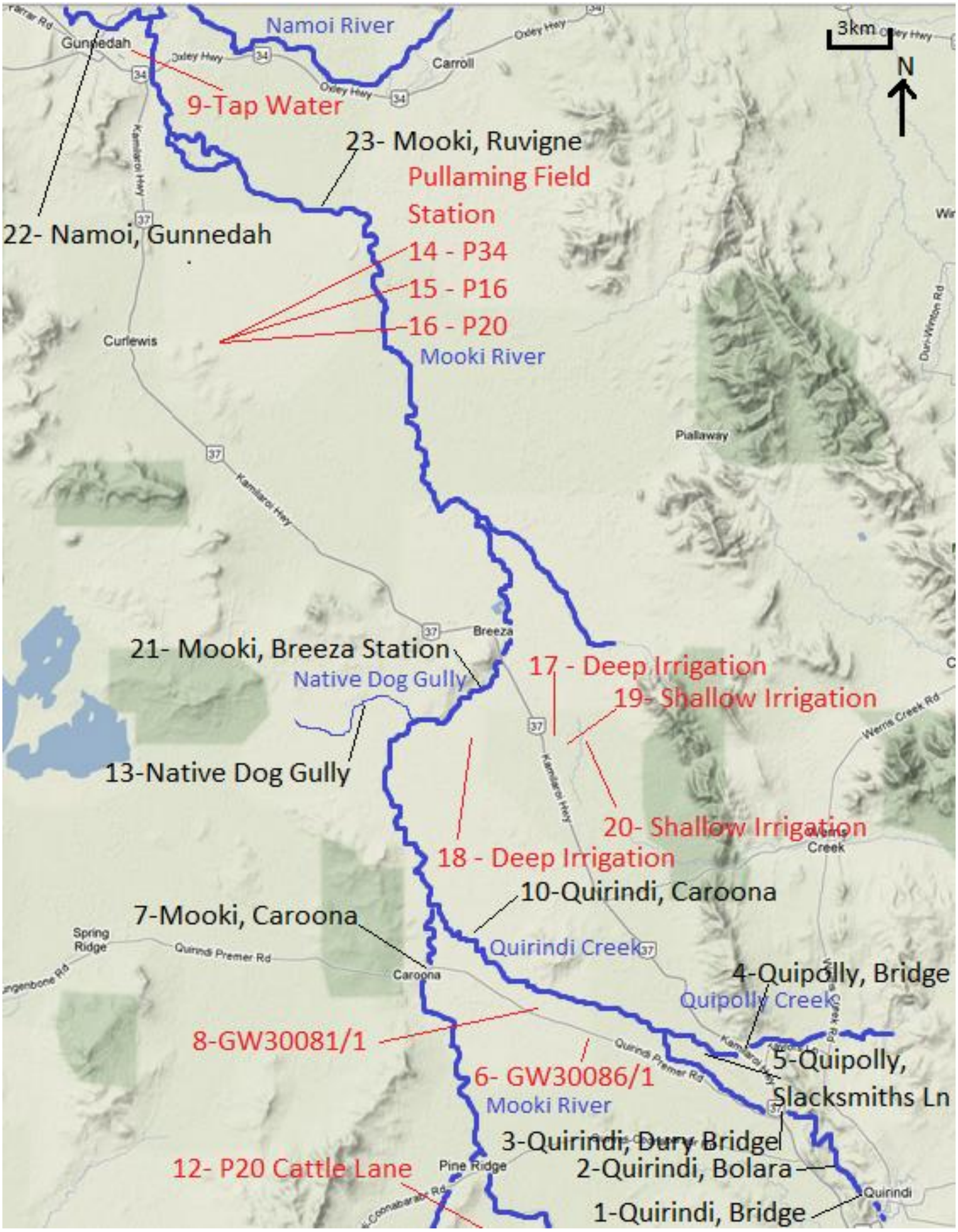
Appendix 1: Map of Sample Locations



Appendix 2: Table of Samples

All values expressed in mg/L unless otherwise indicated

Sample #	River/Creek	EC (µS cm^{-1})	pH	Temp (°C)	Na	Mg	Ca	K	Cl	SO$_4$	HCO$_3$
1	Quirindi	1276	7.61	22.3	86.6	56.0	86.5	1.89	109	114	401.38*
2	Quirindi	1298	8.06	24.9	90.6	55.9	83.9	2.83	116	104	448.91
3	Quirindi	999	7.96	23.8	91.8	56.9	82.5	3.76	114	95	468.76
4	Quipolly	955	7.48	24.3	71.9	28.1	61.7	1.84	122	27	265.96*
5	Quipolly	988	7.99	24.9	77.4	29.3	63.8	3.45	127	21	275.72*
6	GW30086/1	929	7.27	20.9	48.1	42.7	71.4	1.87	94	82	295.80
7	Mooki	1211	6.71	24.3	104	74.9	54.3	4.35	189	17	401.38*
8	GW30081/1	4550	6.72	19.7	513	233	251	2.21	1557	236	318.78
9	Tap Water	511	6.83	24	33.9	22.9	45.2	1.12	48	42	200.08*
10	Quirindi	883	6.81	19.7	76.6	44.0	67.0	7.36	98	41	419.02
11	Mooki	1061	6.82	22.5	74.9	58.6	41.0	3.14	122	16	392.03
12	P20	/	/	/	1655	356	135	3.50	3482	297	232.35
13	Native Dog Gully	17460	6.81	23.6	2788	761	258	16.6	6208	1479	0.00**
14	P34	4450	6.75	22.9	154	22.9	31.1	1.78	169	105	196.96
15	P16	4220	6.79	21.6	206	18.6	30.3	1.71	140	56	421.44
16	P20	1147	6.76	20.5	200	26.9	45.2	1.92	176	50	438.66
17	Deep Irrigation	759	6.78	20.3	72.1	30.9	56.7	2.39	69	29	344.04*
18	Deep Irrigation	712	6.76	20.6	56.2	33.1	59.3	2.37	43	17	372.10*
19	Middle Plain	1201	6.77	20.5	153	34.7	37.3	2.13	144	40	374.54*
20	Black Dam	1929	6.79	19.8	368	16.8	14.4	0.85	237	126	507.52*
21	Mooki	1462	6.8	24.9	121	66.5	56.2	5.70	229	26	407.40
22	Namoi	263.5	6.82	22.4	14.5	8.90	17.3	2.99	12	12	103.94
23	Mooki	688	6.84	23.2	65.9	35.0	37.6	5.76	100	16	282.35

*Samples had bicarbonate analysed. All other samples did not have bicarbonate analysed and was back-calculated assuming an overall ion balance of 0.

**Native Dog Gully required higher positive charge, indicating absence of cation. HCO$_3$ left as 0.

Appendix 3: Driller Log

FROM	**TO**	**THICKNESS**	**DESCRIPTION** **All values in metres**
0.00	3.05	3.05	Clay Dark Brown
3.05	4.57	1.52	Clay Dark Brown Silt
4.57	6.10	1.53	Clay Fine Sandy
6.10	7.62	1.52	Clay Fine-medium Sandy
7.62	9.14	1.52	Clay Silty
9.14	10.67	1.53	Clay Silty Some Fine Sand
10.67	13.72	3.05	Clay Silty Water Supply Jasper Sub Rounded Gravel Fine Pebbles/pebbly Some Fine-coarse Sand
13.72	15.24	1.52	Clay Silty Water Supply Some Fine Sand Gravel Fine Pebbles/pebbly
15.24	16.76	1.52	Clay Fine-medium Sandy Water Supply Gravel Fine Pebbles/pebbly
16.76	19.81	3.05	Clay Fine-medium Sandy Water Supply
19.81	21.34	1.53	Some Fine Gravel Rock Fragments Sub-rounded Rock Fragments Sub-rounded
21.34	22.86	1.52	Sand Medium-coarse Silt Water Supply Some Fine Gravel Rock Fragments Sub-rounded Gravel Medium Pebbles/pebbly Fine Sand
22.86	24.38	1.52	Clay Fine Sandy Silt
24.38	25.91	1.53	Gravel Fine Silt Rock Fragments Sub-angular/sub-rounded Some Clay Gravel Medium Pebbles/pebbly

Stratigraphic log for GW30000 at Breeza. Source: Groundwater Works.

Appendix 4: Organics Summary

Chemical All figures in ng/L	# sites detected Jan (n=22)	Max Conc detected	# sites detected Oct (n=12)	Max conc detected	Aus. Drinking Water Guidelines 6	ANZECC Aquatic Ecosystem Guidelines	ANZECC Primary Industries Guidelines	Detection limit	Use/Source	Degredation
ibuprofen	1	7	0	\	x	x	x	5	Anti-inflammatory	photolytic
triclosan	2	10	0	\	x	x	x	5	Toothpaste	Photolytic
t-octylphenol	8	322	1	368	x	x	x	10		Microbial
polyparaben	12	1600	7	216	x	x	x	10	Cosmetics	
phenylphenol	5	471	4	257	x	x	1,000,000	10	Disinfectant	Microbial
nonylphenol	0	\	6	137	x	ID	x	5	Detergents	Microbial
Paracetamol	3	31	2	26	x	x	x	5	analgesic	rapid photolytic
Sulfamethoxazole	1	58	0	\	x	x	x	5	Antibiotic	Photolytic
Caffeine	18	272	5	249	x	x	x	10	Stimulant	Multiple
TCEP	8	61	5	11	x	x	x	5	Reducing Agent	conservative
Dilantin	1	6	0	\	x	x	x	5	antiepileptic	
Carbamazepine	2	10	0	\	x	x	x	5	anticonvulsant	
Enalapril	4	42	0	\	x	x	x	10	blood pressure	?
Risperidone	8	156	0	\	x	x	x	5	antipsychotic	Conservative
Atrazine	17	5000	9	763	20,000	700 (99%)	10,000	5	herbicide	Conservative
DEET	11	46	8	313	x	x	x	5	Herbicide	Conservative
primidone	2	14	0	\	x	x	x	5	anticonvulsant	Conservative
Verapamil	1	18	0	\	x	x	x	5	bloodpressure	Photolytic
Simazine	8	210	N/A	N/A	20,000	200 (99%)	10,000	5	Herbicide	Photolytic

Table 1: Summary of trace organics. For purposes of brevity, only analytes above the detection limit are displayed. Those tested for and omitted are: ketoprofen, naproxen, gemfibrozil, simvastatin-hydroxyacid, simvastatin, diclofenac, triclocarban, nonylphenol, atenolol, trimethoprim, p-hydroxyAtorvastatin, Fluoxetine, o-hydroxyAtorvastatin, Linuron, Atorvastatin, omeprazole, clozapine, amitriptyline, triamterene, meprobamate, hydroxyzine, diazepam.

Appendix 5: Field photographs

Photo 1: Dry section of Quirindi Creek

Photo 2: Waste Treatment plant at Quirindi