Water and sediment quality in the Diamantina-Georgina River catchment, Lake Eyre Basin

Mike Williams, Rai Kookana, Sheridan Martin,
Jun Du, Danni Oliver and Jim Cox

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Enquires should be addressed to: Goyder Institute for Water Research
Level 1, Torrens Building
220 Victoria Square, Adelaide, SA, 5000
tel: 08-8303 8952
e-mail: enquiries@goyderinstitute.org

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Glossary and Definition of Acronyms and Terms

Al	Aluminium
ANZECC	Australia and New Zealand Environment and Conservation Council
ARMCANZ	Agriculture and Resource Management Council of Australia and New Zealand
As	Arsenic
Cl	Chloride
DO	Dissolved oxygen
EC	Electrical conductivity
fDOC	Fluorescent dissolved organic carbon
Fe	Iron
K	Potassium
LEB	Lake Eyre Basin
MST	Microbial source tracking
N	Nitrogen
Na	Sodium
NH_3/NH_4^+	ammonia/ammonium (protonated form of ammonia)
NO_3^-	Nitrate
NO_2^-	Nitrite
NO_x	Oxides of nitrogen (sum of nitrate/nitrite)
NTU	Nephelometric turbidity units
P	Phosphorus
pH	measure of acidity (concentration of hydrogen ions)
PO_4^{3-}	Phosphate
Queensland DNRM	Queensland Department of Natural Resources and Mines
S	Sulfur
SA EPA	South Australian Environmental Protection Authority
SO_4^{2-}	Sulfate
Zn	Zinc

Executive Summary

The Lake Eyre Basin (LEB) covers around 1.2 million km^2 in the arid region or 15% of the Australian, with livestock grazing comprising around 80% of land use, and around 10% of land set aside for conservation. Extractive industries (e.g. gas and oil) and tourism are other significant industries in the LEB, although their land-use footprint is considerably less than livestock. The LEB has a low population density with around half of the total population in the basin (approx. 60,000) located in the urban centre of Alice Springs. The rivers within the LEB sub-catchments are largely unregulated, with minimal extraction and diversion of water bodies. Seasonal inundations and high variability in water flows are among the key features of the basin. Disconnected waterholes play a critical ecological role during periods of no rainfall and have relatively high rates of primary production (mainly algae sustaining the food web). These waterholes are therefore important in supporting resident fauna and flora.

Monitoring of water quality in the LEB by state agencies over the last four decades has noted elevated levels of nutrients and turbidity, often exceeding existing ANZECC water quality guidelines
A Goyder Institute-funded project was therefore developed with the following aims relating to nutrient dynamics and their potential sources (Task 4 of the overarching project):

1. To undertake a desktop review of existing available water quality data within the LEB.
2. To conduct a field-based water and sediment quality assessment in the areas identified during the desktop review and add to, or compare with, the historical data.
3. To review the commonly used source-tracking markers and utilise these, if possible, to identify the potential sources of contamination in the LEB during field monitoring program
4. To make recommendations for future monitoring programs based on the project findings.

Review of existing data on nutrients in LEB

A review of existing water quality data for LEB revealed that monitoring of water quality in the LEB has been carried out at a number of sites over the last four decades by state-based government agencies and have variously measured a number of water quality parameters. Some data was also available from peer-reviewed literature.

The review found that the available data, primarily related to water quality parameters such as nutrients (particularly N and P), turbidity, pH and electrical conductivity (EC), was collected inconsistently and only available for a limited number of sites within the LEB. The predominant source of these data was the Queensland Department of Natural Resources and Mines (DNRM) and the SA Environmental Protection Authority (EPA). The methodology for obtaining the water quality data (e.g. sampling procedure, analytical methodologies) was not easily available from these sources, which can have implications for consistency in comparisons with historical data.

From the available monitoring data within the LEB, it is apparent that a number of water quality parameters such as nutrients and turbidity are often elevated, when compared with the current water quality guidelines developed for the Australian environment (ANZECC/ARMCANZ 2000) as a benchmark. Guideline trigger values apply to parameters such as total nitrogen (N), total phosphorus (P), biologically relevant species of N and P, pH, dissolved oxygen, chlorophyll A, turbidity and salinity, as adapted for low rainfall areas of south central Australia. While N, P and turbidity generally exceeded the guideline values, the other water quality parameters, such as pH, EC (also related to salinity), dissolved oxygen (DO) and a number of trace elements were generally found in the acceptable range.

Water and sediment sampling in Georgina-Diamantina catchment

The Georgina-Diamantina River catchment was selected for a once-off longitudinal sampling campaign for water quality, based on the literature review. The site selection within the system was guided by previous water quality, biological and/or hydrological monitoring. Due to the highly ephemeral nature of water flow in the system, targeting previously assessed sites increased the likelihood of finding water for collection, although this was still not the case for the southernmost sampling sites. Water and sediment samples were sampled for determination of physical parameters (pH, EC, DO, redox status, turbidity, alkalinity), nutrient levels (N, P, S), trace element concentrations and potential markers of particular land uses (*see* Tracers to identify contaminant sources), with analysis undertaken both *in situ* and in the laboratory.

Water quality

Concentrations of nutrients, including total and biologically utilisable forms, were often found to be elevated and exceeding the ANZECC/ARMCANZ water quality guideline trigger values relevant to basin conditions. Concentrations of total N exceeded the guideline value of 1 mg/L at 4 of 14 sites, while biologically utilisable forms of nitrogen, nitrate (NO_3^-) and nitrite (NO_2^-) (also known as NO_x), were greater than the guideline value of 0.1 mg/L at 11 of the 14 sites. NO_x represented the main N species in the majority of the waterbodies sampled. Total P exceeded 0.1 mg/L at 5 sites, biologically utilisable phosphate (PO_4^{3-}) exceeded 0.04 mg/L at 8 sites and turbidity was above the highest guideline value of 100 NTU at 11 of the 14 sites. These were generally consistent with limited historical data.
Consistent with available historical data collected over the last four decades, the other water quality parameters fundamental for supporting freshwater ecosystems were within guideline values, pH (range 6.5-9), EC (highest value 5000 μS/cm) and DO (90% saturation or ~8 mg/L), indicating the waterbodies had generally very low salinity and good aeration.

Sediment quality

Concentrations of nutrients and trace elements in the sediments were substantially elevated relative to the water column, with concentrations of N, P, C and S in the high mg/kg to low g/kg range. Arsenic (As) was found to be between the trigger (low) and high range of interim ANZECC/ARMCANZ sediment quality guidelines values of 20 and 70 mg/kg at 9 of the 14 sites. Given the link of toxicity with their oxidation state, an assessment of the dominant As, Fe and Al species present in the sediment samples, and their potential toxicological implications, requires further investigation. Soil and manure samples were collected to characterise the potential sources of pollution and compare these with what was measured in sediments. The nutrient and trace element profiles of sediments were found to be similar to that measured in the soil, but the composition of nutrient species (NO_x, NH_4^+ and PO_4^{3-}) were highly variable in both matrices (Appendix 6).

Overall status of Georgina-Diamantina during the survey

Despite the elevated N, P and turbidity levels, a general high degree of oxygenation, low salinity and moderate chlorophyll *a* concentrations were also noted. Elevated concentrations of trace elements such as Al and Zn were consistent with previous sampling data, which also exceeded relevant ANZECC/ARMCANZ water quality guidelines. These results need to be considered in light of the other water quality parameters, such as pH and turbidity. With high levels of clay in the water column and pH values greater than 6 in all waterbodies, it is likely Al (and also Zn) were highly associated with clay, significantly reducing their

bioavailability (and therefore toxicity) to aquatic organisms. To assess the implications of these water quality parameters on the biological health of the ecosystem, however, a targeted assessment of both chemical and biological endpoints in parallel is required.

Tracers to identify pollution sources

Identification of suitable tracers for source tracking in the LEB

A hypothesis tested during this project was that the elevated nutrient concentrations that have featured in water quality monitoring over the last four decades are due to anthropogenic influences. A literature review was therefore conducted of various tracers that have been used for tracking the sources of contamination and to identify those that may be suitable for use within LEB. While a myriad of markers have been used with a varying degree of success in literature, consideration of surrounding land use and defining the expected inputs into the system is necessary to enhance the utility of these methods. For example, a range of sensitive and selective source trackers commonly used in urban settings, such as those associated with sewage, were not considered appropriate due to the low population density in the region. Similarly, source tracers linked with inputs of fertilisers were also deemed unsuitable. With around 80% of the LEB under livestock grazing, tracers relating to animal sources of contamination were considered to be more relevant. These included source tracers relating to chemical and microbiological inputs. Microbial source tracking (MST) is becoming increasingly attractive in tracking waste derived from various livestock, being highly sensitive and selective, and can include directly counting/identifying microorganisms (including bacteria and viruses), assessing genetic biomarkers, metagenomics assays or measuring chemical signals from specific pathways. Indirect assessment of microbial activity derived from wastewater streams includes measuring the fluorescence intensity of dissolved organic carbon (DOC), which can differentiate between microbially-derived DOC and plant-derived DOC. Assessment of chemical inputs usually relates to mammalian hormones and sterols with the presence of these cholesterol-derived chemicals, as well as the ratio of various hormones and sterols, indicative of inputs from mammals. Not all of these tracers, however, may be suitably sensitive or selective depending on the extent of inputs into the system and the environmental conditions of the system. It is therefore desirable to include a number of different tracers to enable greater confidence in source apportionment.

Monitoring source tracking parameters in Georgina-Diamantina catchment

Based on the literature review, two different tracers were measured during the water and sediment monitoring campaign to assess the potential influence that livestock could have on the waterbodies. These were steroid hormones (including a number of estrogens and androgens) and the fluorescence signal of DOC (fDOC).

Hormones were generally not detectable at the majority of sites. An androgenic hormone, androsterone, was found in the water column at 6 of the 14 sites. Another estrogenic hormone, estrone, was found only in sediments, where it was present at 7 of the 14 sites and not necessarily corresponding with androsterone in the water column.

For fDOC, microbially-derived DOC was elevated at some sites compared with others. Other water quality data, however, did not show any trends with respect to the elevated levels of fDOC.

There was widespread evidence of cattle at sampling sites (particularly tracks and dried manure) which suggests the hormone and fDOC signals may have been related to animal-derived inputs but this could not definitively assign livestock as the source of elevated nutrients in the waterbodies.

Conclusions and Recommendations

- Water quality data in LEB were available from the last four decades from a number of sources. However, the available data were generally collected sporadically, at relatively large spatial intervals and focussed on comparatively few measurements, especially nutrient concentrations, turbidity, pH and electrical conductivity. No sediment quality data was found. Sites within the Cooper Creek catchment had the greatest amount of data available. Collated water quality data generally showed elevated nutrient and turbidity values, with respect to ANZECC/ARMCANZ national water guidelines, although pH, DO and EC were within guideline values.
- A once-off sampling campaign in spring 2014 in the Diamantina-Georgina River catchment found nutrient levels were found to exceed ANZECC/ARMCANZ water quality guideline trigger values at the majority of sites. These were generally consistent with collated historical water quality data.
- The significance of water quality parameters exceeding national guideline values is difficult to evaluate in the absence of additional chemical assessments (e.g. chemical speciation of trace elements) or of concurrent biological surveys in the sampled waterholes.
- A number of parameters were identified as being suitable for tracking sources of potential pollution in LEB, based on livestock grazing being one of the most widespread land uses. Hormones and the fluorescence signal of dissolved organic carbon (fDOC) were not able to definitively link livestock grazing with elevated nutrient inputs into waterways. More work is therefore needed to establish the likely sources (e.g. animal activity) or causes (e.g. evaporation) of nutrients in LEB streams.

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Introduction

Lake Eyre Basin

Australia has a land surface area comprising of around 70% classified as semi-arid or arid lands, where less than 350 mm rainfall occurs annually. The Lake Eyre Basin (LEB), itself covering around 1.2 million km^2 or 15% of the Australian continent, sits within this arid region (Department of the Environment 2015). The LEB consists of a number of river systems, including the Neales-Peake catchment in the northwest of the basin and the Cooper Creek and Diamantina-Georgina catchments in the eastern LEB, which sporadically drain into Lake Eyre (or Kati Thanda). Within this arid region, the river catchments often consist of disconnected waterholes for long periods that can be connected during infrequent inundations, usually originating from seasonal monsoonal precipitation in the upper regions of the catchments (Silcock 2009). When inundation occurs, the water flows can be substantial, such that the variability in water flows in the Diamantina and Cooper catchments are among the most highest in the world (Arthington and Balcombe 2011; Puckridge et al. 2010; Sheldon and Fellows 2010). Because of the arid conditions and "boom and bust" cycles occurring in the LEB, the disconnected waterholes play a critical ecological role during periods of no rainfall and the waterholes have relatively high rates of primary production (by Australian standards) with populations of algae providing a fundamental basis for sustaining food webs (Silcock 2009) These waterholes are therefore important in supporting resident fauna and act as refugia for many plant, invertebrate, fish and bird species until periods of high flow occur where productivity and connectivity are at their greatest (Silcock 2009).

Despite the low rainfall experienced throughout the LEB, the region has areas with reliable coverage of edible grass (e.g. *Astrebla*) and non-grass (e.g. sedge) species, with livestock grazing one of the major industries supported within the basin in terms of land use area. Livestock grazing covers around 80% of land use within the LEB, with extractive industries (e.g. gas and oil) and tourism, having a significantly smaller geographical footprint (Environment 2015). Although only around 10% of land use in the LEB is set aside for conservation, the rivers within the catchments are largely unregulated, with minimal extraction and diversion of water bodies (Costelloe et al. 2006). The population of the LEB is around 60,000, around half of which is located in the urban centre of Alice Springs, and settlements are widely dispersed and population density is subsequently low. This indicates that urban pressures on surface water quality are also likely to be low.

Water quality in the Lake Eyre Basin

The Lake Eyre Basin rivers assessment (LEBRA) is a federal monitoring program, assessing the condition of fish populations, hydrology and water quality in LEB. One of the aims of assessing water quality is to ensure measured water quality parameters are in accordance with required ranges to support resident fauna and that monitoring water quality is a rapid and quantifiable means of determining whether these ranges are exceeded (Sternberg et al. 2014). Monitoring of water quality in the LEB has occurred at a number of sites over the last four decades by state-based government agencies and have variably measured a number of water quality parameters, usually including pH, nutrients, salinity and turbidity. To provide a benchmark against which these collated water quality parameters can be compared, current water quality guidelines developed for the Australian environment can be used. National water quality guidelines published by the Australian and New Zealand Environment and Conservation Council (ANZECC) and the Agricultural and Resource Management Council of Australia and New Zealand (ARMCANZ) in 2000 provide a range of relevant water and sediment quality parameters for a range of different purposes, including aquatic ecosystem

health, use in agriculture and recreational activities (ANZECC/ARMCANZ 2000). Default guideline values for physicochemical stressors (nutrients, chlorophyll *a*, turbidity, dissolved oxygen, pH and salinity) have been derived from data obtained through monitoring programs around Australia (and New Zealand). The overall aim of the water quality guidelines is to give a value of a potential stressor that enables resource managers to make appropriate decisions to mitigate the effect of the stressor. In general, guideline trigger values can be derived from 80th (and/or 20th) percentile values obtained from data collated over a set period of time at an appropriate reference site (ANZECC/ARMCANZ 2000). These guideline trigger values have been adapted for particular geographic regions in Australia, including low rainfall areas of south central Australia. For toxicants, such as trace elements, species sensitivity distributions from collated ecotoxicity data is used to estimate a certain percentage of species would be protected. Protection values are variable and greater than 80% depending on the desired management outcomes with, for example, a 95% protection level generally applied to a slightly to moderately disturbed system. Sediments generally have had considerably less assessments undertaken compared to water, in terms of monitoring and scientific understanding of stressors and toxicants, and there is subsequently less data available for effective sediment quality guideline values (ANZECC/ARMCANZ 2000).

Previous monitoring data for waterbodies within the LEB have indicated that a number of water quality parameters, such as nutrients and turbidity, are often elevated and can exceed existing default trigger values (Sheldon and Fellows 2010; Sternberg et al. 2014). High turbidity is often an indication of poor water quality (ANZECC/ARMCANZ 2000) while the levels of N and P measured in the LEB waterways is in the same range as is found in treated sewage (e.g. Higgins et al. 2004). This raises the question of whether the measured parameters represent true baseline values for waterbodies in the LEB or whether the aquatic ecosystems are disturbed leading to potential stressors exceeding guideline trigger values. Also, if the LEB aquatic ecosystems are disturbed, what are the reasons for the disturbance and can decisions be made to mitigate the apparent disturbances to the system? This needs to be considered in the context of the waterbodies in the LEB being subjected to extremes in climatic and hydrological conditions, which can have a significant impact on water quality parameters. For example, under conditions of flooding and high flow, nutrient concentrations have been found to be lower than under no flow conditions when waterholes are disconnected (Sheldon and Fellows 2010).

Based on these elevated nutrient concentrations found in literature, a wider review of available water quality data for the LEB was undertaken to determine whether elevated concentrations of nutrients are historically and geographically consistent. Alongside nutrient data, other water quality data were also included in the review when available as a means of assessing the condition of waterbodies. In conjunction with a desk-based assessment of water quality parameters, a longitudinal water quality monitoring campaign was undertaken in a sub-catchment of the LEB. As there are relatively less data available in the Diamantina and Georgina River catchments of the LEB, sampling was targeted in this catchment. Longitudinal sampling of river systems allows an assessment of where various geographical and anthropogenic influences occur as a river travels downstream although it should be noted that for the period of the sampling campaign all of the waterbodies sampled were discrete entities, disconnected from other upstream and downstream waterbodies. Since the sampling consisted of a single temporal period, the no flow conditions was considered to be representative of a worst-case scenario, *in lieu* of a more desirable sampling campaign over a greater temporal range. To assess potential anthropogenic impacts within the sampled sub-catchment, a number of additional water quality parameters were measured that may relate to land use activities that may be indicative of an impacted aquatic ecosystem. These included natural hormones, organic carbon related to microbial activity and trace elements, which may be derived from activities such as livestock grazing and extractive industries. Also, sediments were included in the sampling campaign, since sediments can temporally accumulate a number of stressors, compared with water columns where greater turnover of these stressors can occur. Furthermore, with a paucity of data relating to sediment quality in the LEB

characterisation of sediments may contribute to the condition assessment of rivers in the LEB and understanding of sediment quality in Australia.

Objectives

Specifically, the project objectives included:

- Conducting a literature review of available data on water (and sediment) chemistry in the LEB and collating the ranges of values to provide an assessment of whether elevated concentrations of nutrients occur throughout the LEB and over a period of time.
- Identification of water quality parameters that could be used to apportion sources of elevated chemical stressors, such as nutrients, in the LEB aquatic system. This was done in two parts where (i) literature relating to monitoring techniques was used for tracking sources of contamination in waterways and summarising those most suitable for use within LEB and (ii) applying suitable techniques to collected water and sediment samples to determine whether land-use activities within the sub-catchment gave a measurable signal for source apportionment.
- Collection of water and sediment samples along a longitudinal section of the Diamantina-Georgina sub-catchment of the LEB and measure a number of water/sediment quality parameters and compare this with historical data, existing water and sediment quality guideline trigger values. The measurement of sediment quality parameters, in particular, would make an important contribution to datasets that contain little to no sediment quality data.
- To make recommendations for future monitoring of water and sediment quality which can contribute to a consistent and cohesive database and be incorporated within future condition assessments of LEB.

Methods

Historical water quality data

A number of sources were accessed to collate water chemistry data in LEB waterbodies. These included peer-reviewed scientific literature sourced through Web of Science, "grey" literature (on-line reports and websites relating to LEB) and government agency databases, such as the Bureau of Meteorology (http://www.bom.gov.au), South Australian Environmental Protection Authority (SA EPA) and Queensland Department of Natural Resources and Mines (DNRM) water monitoring portal (http://www.dnrm.qld.gov.au). All aspects of water quality were collated (where available) including physical parameters, such as pH, salinity, turbidity and dissolved oxygen, and chemical water quality parameters, such as nitrogen, phosphorus, major cations and trace metals.

Nutrients - water and sediment sampling

Water and sediment samples were collected from 29th August through to 6th September 2014 from a number of sites within the catchment (Figure 1, Appendix 1). An interactive version of the sampling sites, summarising location, photos and water and sediment chemistry data can also be accessed through Google Earth (https://sites.google.com/site/csirowaterqualitypilot/). Sampling sites were based on those that have been previously selected for biological and hydrological monitoring (Sternberg et al. 2014), were expected to have water due to their status as permanent water holes (Silcock 2009) or had previous water quality data available for comparison. The northern boundary of the sampling campaign were collected from near Boulia in the Georgina catchment and near Winton in the Diamantina catchment, with sampling continuing longitudinally along both rivers, with Cowarie Station (on the Warburton River) in South Australia and Mungerannie Station (on the Derwent Creek) defining the southern sampling boundary.

Water samples were collected in triplicate at each site from within 2 m of the water's edge, with general water quality parameters, nutrient levels, trace element concentrations and potential markers of particular land uses measured in collected samples (Table 1). Water quality parameters included acidity (pH and alkalinity), degree of oxygenation (dissolved oxygen and redox potential), turbidity and temperature. Total nutrient levels, such as nitrogen (N), phosphorus (P) and sulfur (S), were measured in collected samples along with biologically utilisable species, such as nitrate/nitrite (NO_3^-/NO_2^- or NO_x), ammonium (NH_4^+) and phosphate (PO_4^{3-}). A full list of water quality analytes and their analytical methods is summarised in Table 1. A number of the parameters were measured *in situ*, although measurement of most analytes required samples to be stored and appropriately preserved for laboratory analysis at a later date. Preservation processes were variable and dependent on the particular analyte, with a summary given in Table 1. Details on water collection methodology are given in Appendix 2.

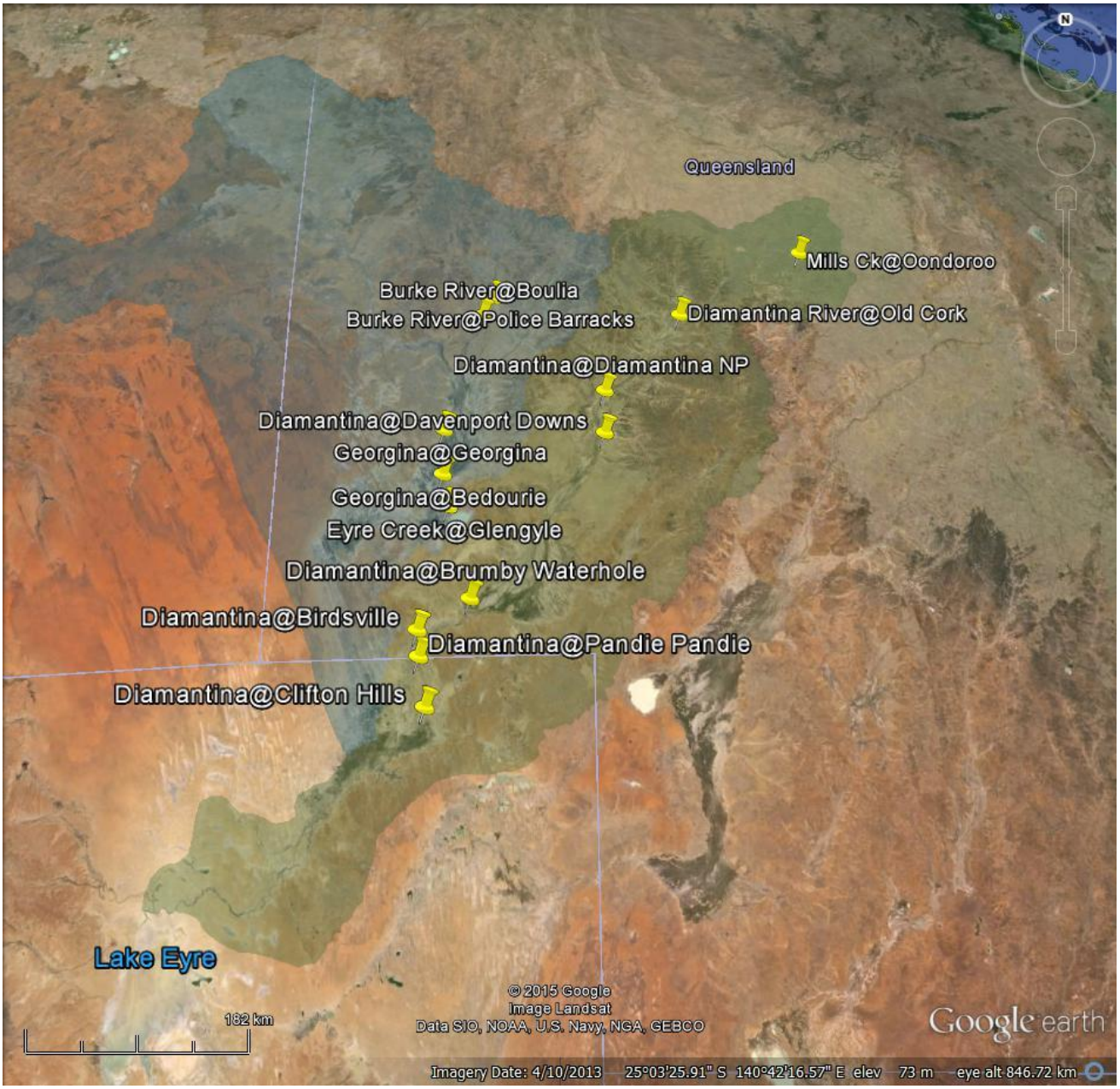

Figure 1. Location of sites sampled during September 2014. Blue shading represents the Georgina Basin and green shading represents the Diamantina Basin. More details of each site are given in Appendix 1 as well as through https://sites.google.com/site/csirowaterqualitypilot/, including full water and sediment quality data obtained from sampling (image courtesy of Google Earth).

Sediment samples (to ~50 mm depth) were collected in triplicate along with water samples, with sediment analyses undertaken both *in situ* and in the laboratory. Due to available analytical capabilities, the range of analytes for the sediment samples was less than that of water samples (Table 1). Inclusion of analyses of sediments can give a better indication of the overall quality of the sampled water bodies, since sediments can act as a sink for nutrients found in water bodies (Reddy et al. 1999; Vought et al. 1994). Soil (~50 mm depth) and manure (sub-sampled from within the crust of the manure) samples were also collected at each site for nutrient and trace element analysis.

Source tracking - water and sediment sampling

Based on historical water quality data, there was an expectation of elevated nutrient concentrations in the collected water samples and indicators of potential impacts on the catchment were therefore also measured. This was done to assess whether the high nutrient levels previously determined in the LEB could be attributed to land-use activities within the catchment. Since land use within the LEB is predominantly cattle grazing, two analytical procedures were used to assess the potential influence that cattle could have on the waterbodies. Over a period of a day, cattle are often found close to waterbodies, with this increasing where water resources were limited and daytime temperatures were high (Pandey et al. 2009). Cattle can excrete appreciable quantities of hormones in urine and faeces which can lead to contamination of waterways (Kolodziej and Sedlak 2007). Due to the chemical nature of hormones, they often associate to a greater extent with sediments (e.g. Kolpin et al. 2013, Kuster et al. 2004) which further emphasises the need for sediment sampling during the campaign.

Digestion of feed in cattle involves considerable microbial activity, with microbial endpoints also used to assess impacts of cattle on waterways (Furtula et al. 2012). A chemical measurement of microbial activity included in this sampling campaign was a measurement of the fluorescence spectrum of dissolved organic carbon (fDOC) and has previously been used to track wastewater contamination (Henderson et al. 2009; Hudson et al. 2007). Organic carbon derived from microbial sources is often high in protein-derived tyrosine and tryptophan-like organic carbon, which has a distinctive fluorescence spectrum from organic carbon-derived from plant material, rich in humic and fulvic acids (Baker 2002). Details of sample collection methods and analysis are summarised in Table 1 and Appendix 2. Other relevant activities within the LEB also include tourism and extractive industries. The presence of hormones and microbially-derived DOC was also considered relevant to presence of human activities related to tourism.

This may also be relevant to settlements within the LEB associated with extractive industries, although this is not extensive within the Diamantina and Georgina River catchment area. Wastewater from gas extraction processes often has elevated concentrations of salts and trace elements, derived from water associated with coal or shale deposits, and any overflow into surface water would be expected to give an enhanced level of salinity, ions associated with salinity (e.g. sodium, carbonate and chloride ions) and trace elements (Alley et al. 2011; Batley and Kookana 2012)

Based on population levels and land-use activities, previously used tracers of human activity relating to sewage discharges (such as pharmaceuticals and personal-care products) and agricultural activities (such as pesticides) were not considered.

Table 1. Summary of parameters monitored in water and sediment samples, including the analytical methodology used

Parameter	Analyte	Unit	Method
Water and sediment quality parameters	pH	n.a.[a]	Field (probe)
	Redox potential	mV	Field (probe)
Water quality parameters	Turbidity	NTU	Field (probe)
	Total dissolved solids (TDS)	mg/L	Field (probe)
	Conductivity	μS/cm	Field (probe))
	Salinity	mg/L	Field (probe)
	Dissolved oxygen (DO)	mg/L	Field (probe)
	Alkalinity	mg/L	Field (titration)
Nutrients (water and sediment)[b]	N, NH_4^+, NO_x	mg/L mg/kg	Laboratory (various)
	P, PO_4^{3-}	mg/L mg/kg	Laboratory (various)
	C, organic C	mg/L mg/kg	Laboratory (various)
	Cations (Na, K, Ca, Mg)	mg/L mg/kg	Laboratory (ICP-MS[c])
	Anions (Cl^-, SO_4^{2-})	mg/L mg/kg	Laboratory (various)
	Trace elements (30 total)	mg/L mg/kg	Laboratory (ICP-MS)
Hormones (water and sediment)	Androsterone Androstenedione Dihydrotestosterone 17α-Estradiol 17β-Estradiol Estriol Estrone	mg/L mg/kg	Laboratory (GC-MS/MS[d])
fDOC (water)	DOC	n.a.	Laboratory (fluorescence spectroscopy)

[a]not applicable; [b]nutrients measured as aqueous extracts of sediments; [c]inductively coupled plasma mass spectrometry; [d] gas chromatography tandem mass spectrometry

Results

Historical data

The availability of water quality data for sites within the LEB was quite variable with the types of parameters measured dependent on the data source. With respect to scientific peer-reviewed literature, data were generally limited since water quality assessment was not a principal aim of the collated papers. Often water quality was measured in conjunction with other condition assessments, such as macroinvertebrate populations and primary production within waterbodies (e.g. Choy et al. 2002, Fellows et al. 2007). One exception to this was a study by Sheldon and Fellows (2010), who assessed the influence of spatial and temporal variability, including the effects of water flows, on water quality parameters in the Cooper Basin. Water quality parameters were limited to total N and P, pH, EC, turbidity, hardness, total dissolved solids (TDS) and total suspended solids. Another study in the Cooper and Diamantina catchments included pH, EC, turbidity, dissolved oxygen (DO) and total P and N at each waterhole assessed (Long and Humphery 1995). This monitoring of water quality was used as a means of providing a foundation for a condition assessment of fish populations at selected sites. Water quality data obtained from the Queensland DNRM were similarly limited and included total P and N, NO_3^- and NH_4^+, PO_4^{3-} and DO. The samples were collected from a number of sites in the Diamantina Basin (n=2) and Cooper Basin (n=8). The data collection was sporadic with the number of sampling collection periods ranging from 1-11 at the Diamantina River catchment sites and from 1-48 at the Cooper Creek catchment sites, with collection dates ranging from April 1972 until May 2012. The SA EPA also maintains a water quality sampling database for a number of sites in the LEB, including in the western LEB, in the Diamantina-Georgina catchment and in the Cooper Creek catchment. This database is more diverse in that 16 sites with the South Australian side of the LEB are targeted with up to 225 sampling campaigns taking place at one site (Cullyamurra waterhole in the Cooper Creek catchment). The number of water quality parameters available was also considerable and ranged from physical parameters (including pH, EC, DO), nutrients, trace elements, major cations (including Na, K, Mg, Ca), anions and pesticides. The period of sampling was similar to the Queensland DNRM site, with samples collected between March 1971 and June 2007. The SA EPA also made available water quality data collected in spring 2012.

The collated water quality data are by no means exhaustive, considering the amount of work that has previously assessed the condition of waterbodies within the LEB, and it would be expected that a number of other sites would have relevant water quality data associated with them. It is, however, unlikely that much water quality data exists beyond the early 1970s or if the data would be suitably reliable with considerable advances in knowledge relating to water quality sampling techniques and analysis over the last few decades. The water quality data relevant to the sites targeted in the present monitoring campaign are summarised in Table 2, while a summary of the full data set is in Appendix 4. There were no data available in any of the searched sources pertaining to sediment quality parameters.

In general, nutrient levels and turbidity were elevated at all sites, with N and P (and biologically relevant species of N and P) close to or exceeding default ANZECC/ARMCANZ water quality guidelines in most cases (Table 2, Appendix 4). Conversely, other water quality parameters, including EC, DO and major cations, were not outside guideline ranges. This would indicate that water was generally fresh, moderately alkaline and well oxygenated, despite the eutrophic conditions that the nutrient concentrations would suggest existed. Furthermore, chlorophyll *a* analyses for samples collected in spring 2012 were reasonably low (Table 2, Appendix 4), also supporting elevated nutrient levels not leading to a major disturbance in these waterbodies. An exception to this overall water quality trend in the LEB was noted at two sites in the western LEB, Margaret River and Neales River. These two sites had low NO_x and total P concentrations (<0.1 mg/L) and low turbidity (<50 NTU), while Na, Cl and EC were very high (Appendix 4) indicating very different conditions at these sites. DO levels were still above 8 mg/L at both of these sites. This is consistent with EC,

DO and turbidity data collected in 2012 within the western LEB (Sternberg et al. 2014). The only other site in the western LEB was Yardaparinna Creek, which had turbidity, NO_x, total P and EC more closely aligned with sites in the eastern LEB (Appendix 4).

Where sampling dates were available (e.g. SA EPA monitoring data), there was no consistency noted relating to when samples were collected. For example, sampling data from Birdsville (Diamantina River) spanned from 1971 to 1990 and occurred between February and April, with one sampling campaign occurring in spring 2012 (Appendix 4). Conversely, a site like Cullyamurra (Cooper Creek), which had the most sample numbers in this database and ranged from 1972-2007, had samples collected from all months of the year. With a high degree of variability in LEB catchments, the collection time is likely to play a critical role in the values obtained since flow conditions can have a strong influence on water quality parameters (Sheldon and Fellows 2010). Where sampling dates are noted, it would also be important to consider water flow conditions, which are usually available due to water quality sampling often taking place near water flow gauging stations. Water gauging data are also available through federal agencies such as the Bureau of Meteorology (e.g. http://www.bom.gov.au/waterdata/) for the last 40 years.

Table 2. Historical water quality data (means ± standard deviations) for sampling sites targeted during the present study, with ANZECC/ARMCANZ water quality guideline trigger values. Values exceeding ANZECC/ARMCANZ values highlighted in bold

Site		Diamantina River						Warburton River	ANZECC /ARMCANZ
		Birdsville[a]	Clifton Hills[a]	Davenport Downs[b]	Diamantina Lakes[b,c]	Old Cork[c]	Pandie Pandie[a]	Yelpawaralinna[a]	
Period of sampling		1971-2012	2012	1995	1973-2004	1995	2012	2003-2012	
No. samples		39	1	1	11	1	1	17	
Chlorophyll *a*	µg/L	9.92	15.6	-	-	-	3.53	7.75	-
Nutrients			-	-	-	-	-	-	-
Total C	mg/L-C	20±2.82	-	-	-	-	-	-	-
Organic C		6±5	-	-	-	-	-	30.2±21.7	-
HCO_3^-	mg/L	54.7±15.4	-	-	-	-	-	208±250	-
Total N	mg/L-N		-	-	**1.05±0.64**	-	-	-	1
Total Kjeldahl N (TKN)		**1.4±1.0**	**2.41**	0.7	**1.35**	0.6	**1.71**	-	1[#]
NH_4^+		**0.28±0.29**	-	-	-	-	-	-	0.1
NO_x		0.09±0.04	**1.28**	-	**2.87±1.65**	-	**1.08**	**1.03±0.98**	0.1
Total P	mg/L-P	**0.194±0.029**	**1.02**	**0.69**	**0.48±0.17**	**0.49**	**0.686**	**0.69±0.45**	0.1
SO_4^{2-}	mg/L	9.1±4.49	-	-	-	-	-	30.8±12.5	-
Physical									
Alkalinity	mg/L	44.9±12.6	-	-	-	-	-	170±204	-
Dissolved oxygen (DO)	mg/L	**7.24±0.5**	-	**3.8**	8.62±0.67	**2.6**	-	8.84±1.31	8.2 (@20°C*)
Electrical conductivity (EC)	µS/cm	134±44.8	-	121	90	103	-	1560	100-5000
pH		7.6±0.3	-	-	-	-	-	8.39±0.47	6.5-9 (lower-upper)
Total dissolved solids (TDS)	mg/L	58.5±12.5	-	-	-	-	-	230±180	-
Turbidity	NTU	**557±316**	-	-	-	-	-	**1075±1020**	1-100
Elements[d]									
Aluminium (Al)			-	-	-	-	-	**2.72±4.1**	0.055
Boron (B)		0.07±0.07	-	-	-	-	-	-	0.37
Calcium (Ca)		7.12±3.44	-	-	-	-	-	15.2±4.56	-
Chlorine (Cl)		6±6	-	-	-	-	-	19.6±3.85	-
Copper (Cu)			-	-	-	-	-	**0.022±0.008**	0.0014
Iron (Fe)	mg/L	26.8±28.29	-					36±22	-
Potassium (K)		5.31±3.2	-		3.16±0.8			6.42±2.14	-
Magnesium (Mg)		3.25±1.39	-					5.88±1.35	-
Sodium (Na)		15.6±7.01	-					43.2±16.2	-
Lead (Pb)			-					**0.009±0.004**	0.0034
Silicon (Si)		22.2±14	-					24.2±8.74	-
Zinc (Zn)			-					0.005±0.001	0.008

[a] source:SA EPA; [b] source: Long and Humphrey 1995 [c] source: Queensland DNRM; [d] ANZECC/ARMCANZ value for 95% species protection level [#]NO_x not included in value *DO value dependent on temperature but corresponds with 90% saturation

Water sampling - nutrients and trace elements

Water and sediment samples were collected at all proposed sites except for those south of the Clifton Hills site, which were not suitable for sampling due to either no water being present (Yelpawaralinna and Cowarie Station on the Warburton River) or due to the presence of unrepresentative bore water samples (Mungerranie Station).

The following plots summarise a number of the key water and sediment quality measurements and associated ANZECC water quality guidelines for low rainfall areas in south central Australia (where applicable). All other water and sediment quality parameters are summarised in Appendix 5 and 6.

Consistent with historical data (Appendix 4), values for nutrients including total and biologically utilisable forms of nitrogen and phosphorus were generally elevated and often exceeded ANZECC/ARMCANZ default trigger values (Figures 2 and 3, Table 3). Total phosphorus values were not detectable at a number of sites due to a relatively high limit of quantification (0.2 mg/L). Although there are no relevant default guidelines for chlorophyll *a* in this region, values measured between 1.1±0.7 and 27±22 μg/L were within guideline ranges from other regions of Australia (ANZECC/ARMCANZ 2000). Observations taken during sampling indicated that excessive algal growth, in the form of small algal clumps on the water surface were evident in the northern areas of the Georgina River sampling points (e.g. between Boulia and Bedourie), although this did not lead to an increase in the measured chlorophyll *a* levels at these sites, relative to other sites (Figure 4).

Turbidity was also elevated, as has been consistently found in LEB waterbodies, and generally exceeded the default trigger values (Table 3, Figure 5). Other water quality parameters, including pH (6.45-9.18), electrical conductivity (108-731 μS/cm) and dissolved oxygen levels (>100% saturation) were generally within the trigger values. Redox potential was positive indicating oxidising conditions (Appendix 5).

Of the trace metals, the most notable finding was for dissolved aluminium (Al) and zinc (Zn) in water (Appendix 5). Concentrations of Al in water exceeded the 95% species protection trigger value of 55 μg/L at 11 of the 14 sites, while Zn exceeded its 95% protection value of 8 μg/L at 5 of the 14 sites. Other trace metal concentrations were below guideline values. Where historical data were available for these two elements, the values obtained in the present campaign were found to be consistent with samples collected from previous campaigns (Appendix 4).

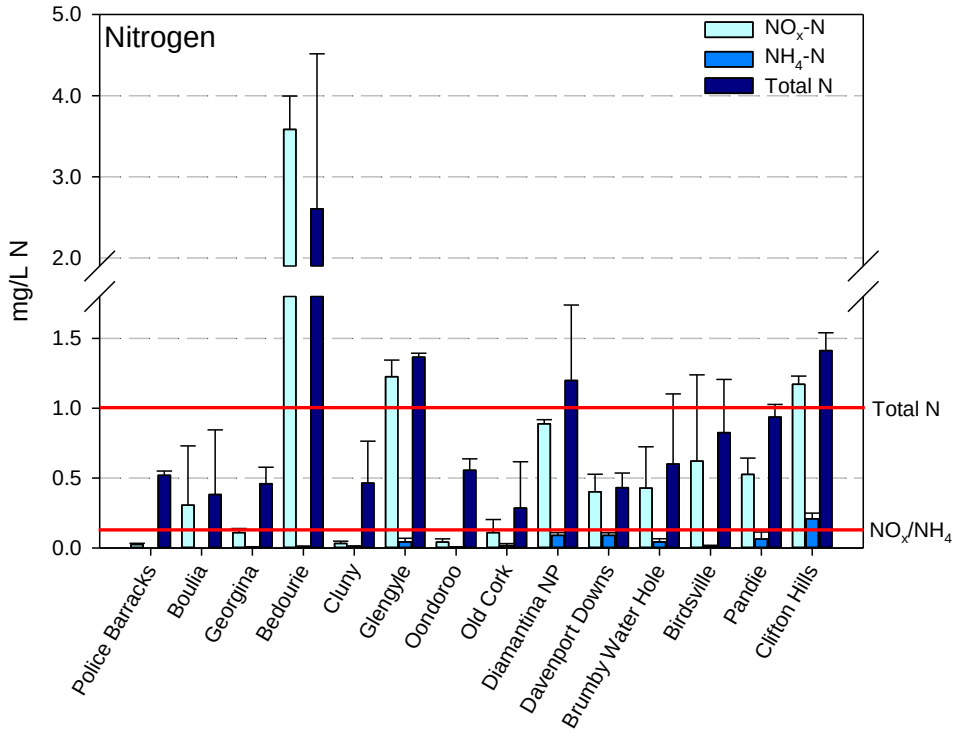

Figure 2. Summary of nitrogen concentrations in water samples, including total nitrogen (N), ammonium (NH_4^+) and the sum of oxides of nitrogen (NO_x). The ANZECC/ARMCANZ default water quality guideline trigger values are highlighted in red for total N, NH_4^+ and NO_x (south central Australia, low rainfall).

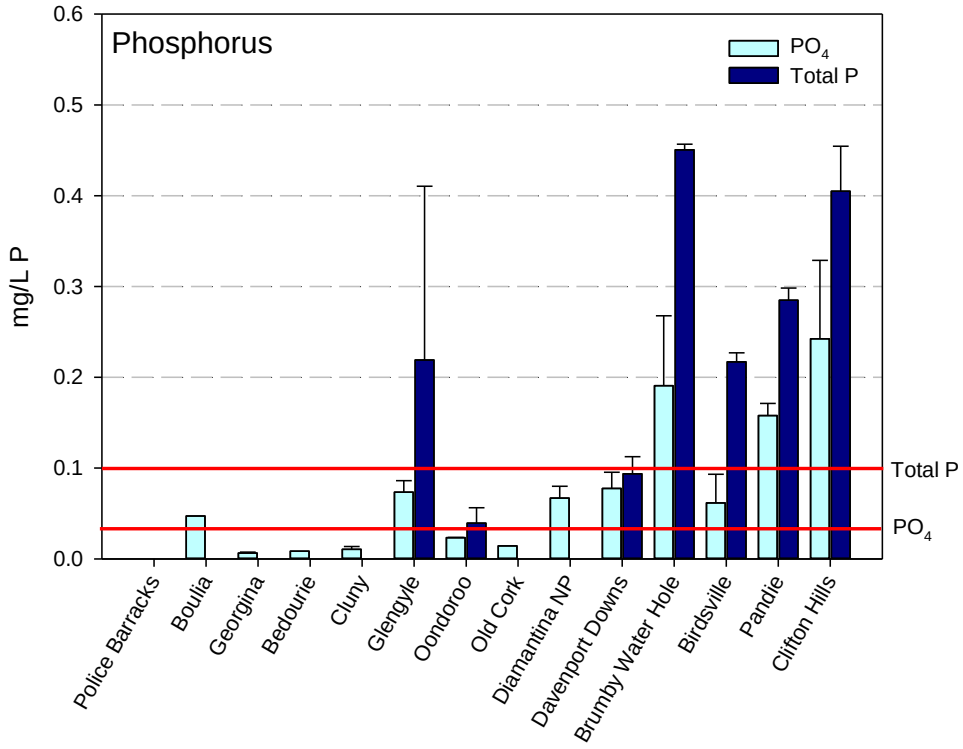

Figure 3. Summary of phosphorus concentrations in water samples, including total phosphorus (P) and monophosphate (PO_4^{3-}). The ANZECC/ARMCANZ (2000) default water quality guideline trigger values are highlighted in red for total phosphorus and PO_4^{3-} (south central Australia, low rainfall).

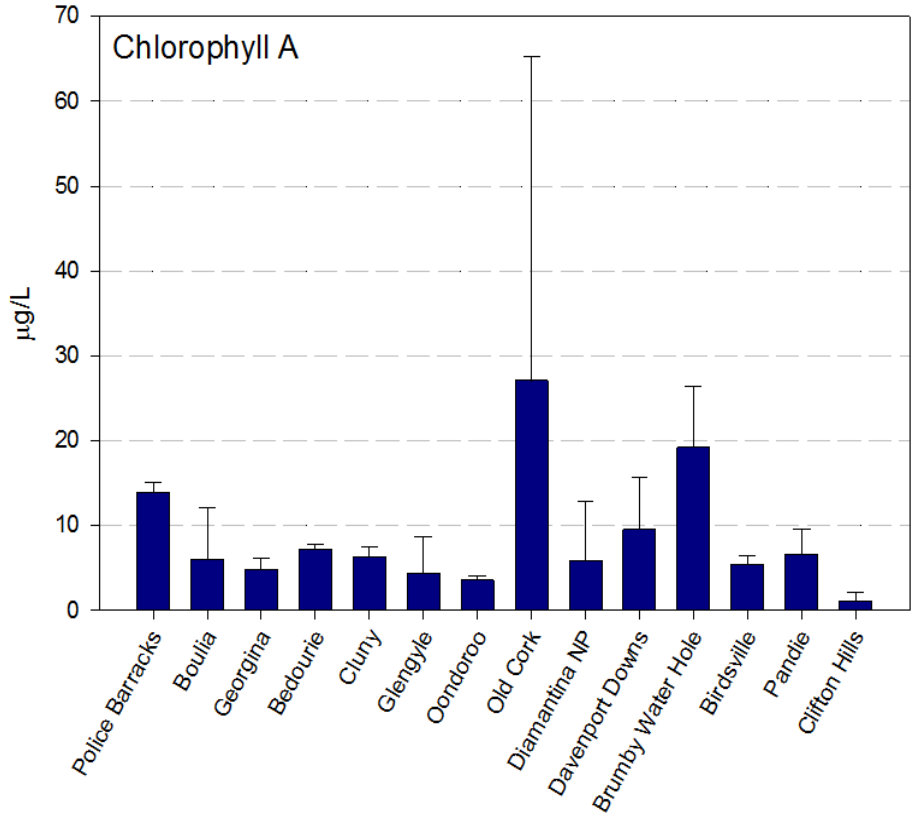

Figure 4. Summary of chlorophyll a concentrations in water samples

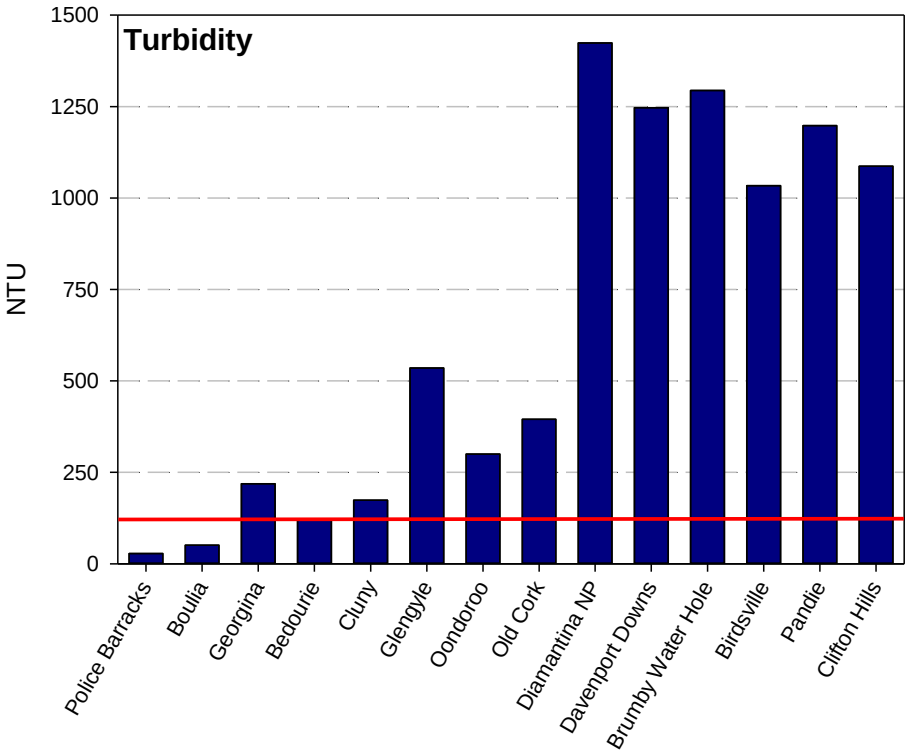

Figure 5. Summary of turbidity concentrations in water samples. The ANZECC/ARMCANZ (2000) default water quality guideline trigger value is highlighted in red for the highest turbidity guideline trigger values (south central Australia, low rainfall).

Sediment sampling - nutrients and trace elements

Analysis of sediments was more restricted in terms of the number of analytes measured and this is also reflected in the ANZECC/ARMCANZ (2000) sediment quality guidelines, which have only a limited number of values for analytes (ANZECC/ARMCANZ 2000). Concentrations of nutrients and trace elements in the sediments were substantially elevated relative to the water column. For example, concentrations for, P, C and S were in the high mg/kg to low g/kg range (Appendix 6). In contrast to N in water, NO_x and NH_4^+ only made up a small fraction of the total N concentration in sediments (Figure 2, Appendix 6).

In general, the pH of sediment was similar or slightly more acidic than water samples. The redox potential was generally lower or negative compared with water, indicating reducing conditions. Organic carbon was generally <1% and constituted the principal form of sediment carbon at the majority of sites (Appendix 6), with the exception of Eyre Creek at Glengyle, where the majority of carbon was present in the form of carbonate. This is in contrast with water samples, where inorganic carbon was found at greater concentrations than organic carbon, although the organic carbon levels in Eyre Creek sediment (0.35%) were similar to other sites (Appendix 6).

Notably high levels of Al and iron (Fe) were present in most sediments, although no guideline values are available for these elements. One element, arsenic, was found to be between the trigger (low) and upper sediment quality guidelines values of 20 and 70 mg/kg respectively at 9 of the 14 sites (Appendix 6).

Electrical conductivity was low at all sites (Appendix 6) and major cations, such as sodium and calcium, and salinity were also found to be correspondingly low (Appendix 6).

Table 3. Summary of sites exceeding highest applicable (south central Australia, low rainfall) ANZECC/ARMCANZ guideline trigger values for water (mg/L) and sediment samples (mg/kg)

Site		Boulia	Georgina	Bedourie	Cluny	Glengyle	Oondooroo	Old Cork	Diamantina NP	Davenport Downs	Brumby Waterhole	Birdsville	Pandie Pandie	Clifton Hills	WQG [a]
WATER															
Nutrient															
Total N	mg/L-N	-	-	2.61±1.91	-	1.36±0.03	-	-	1.2±0.54	-	-	-	-	1.41±0.13	**1**
NH_4^+		-	-	-	-	-	-	-	-	-	-	-	-	0.21±0.04	**0.1**
NO_x		0.31±0.42	0.11±0.03	3.58±0.4	-	1.22±0.12	-	0.11±0.09	0.89±0.03	0.4±0.12	0.43±0.29	0.62±0.62	0.53±0.12	1.17±0.06	**0.1**
Total P	mg/L-P	-	-	-	-	0.22±0.19	-	-	-	-	0.45±0.006	0.22±0.01	0.29±0.01	0.41±0.05	**0.1**
PO_4^{3-}		0.05	-	-	-	0.07±0.01	-	-	0.07±0.013	0.08±0.02	0.19±0.08	0.062±0.03	0.16±0.01	0.24±0.09	**0.04**
Physical															
pH		-	-	9.18	-	-	-	-	-	-	6.45	-	-	-	**6.5-9**
Turbidity	NTU	-	219	-	174	535	300	395	1424	1247	1294	1034	1198	1087	**1-100**
Trace element [b]															
Aluminium (Al)	mg/L	-	-	0.282±0.1	0.16±0.02	0.19±0.07	-	0.21±0.16	0.48±0.13	0.68±0.18	0.75±0.14	0.23±0.08	0.28±0.07	0.4±0.18	**0.055**
Zinc (Zn)	mg/L	-	-	-	0.063±0.01	-	-	-	0.08±0.012	0.078±0.01	0.06±0.005	-	0.11±0.07	-	**0.008**
SEDIMENT															
Trace element															
Arsenic (As)	mg/kg	28±4.5	28±2.6	-	-	-	38±1.2	-	44±3.7	22±1.9	39±1.2	44±1.6	42±5.2	30±4.4	**20-70**

[a] ANZECC/ARMCANZ (2000) default water quality guideline trigger values; [b] ANZECC/ARMCANZ values given for 95% species protection level

Source tracking

Hormones were not detectable at the majority of sites with only an androgenic hormone, androsterone, found in the water column at six sites, ranging from below its limit of quantification (1 ng/L) to 21.6 ng/L (Table 4). Only the estrogenic hormone, estrone, was found in sediments, were it was present at seven sites, ranging from 5.7±1.1 to 34±41 μg/kg (Table 4).

Table 4.Hormones measured in water and sediment samples

Site	Water (ng/L) Androsterone	Sediment (μg/kg) Estrone
Police Barracks (Burke River)	15.1±0.3	-
Boulia (Burke River)	-	9.6±6.7
Georgina (Georgina River)	-	5.7±1.1
Bedourie (Georgina)	20.2±9.5	-
Cluny (King Creek)	13±4.3	8.2
Glengyle (Eyre Creek)	21.6±14.4	-
Oondoroo (Mills Creek)	10±4.5	9.5±6.1
Old Cork (Diamantina River)	-	-
Diamantina NP (Diamantina River)	-	8.7±2.8
Davenport Downs (Diamantina River)	-	-
Brumby Waterhole (Diamantina River)	-	-
Birdsville (Diamantina River)	<LOQ	-
Pandie Pandie (Diamantina River)	-	13.8
Clifton Hills (Diamantina River)	-	34.2±41.2

The excitation-emission spectra (λ_{ex}=300, λ_{em}=350) of fDOC are summarised in Table 5, with a plot of the entire fluorescence spectrum for each water sample in Appendix 8. As a comparative measure, the DOC concentrations measured in the water column were reasonably consistent across all sites, although elevated levels (>100 fluorescence units) were noted at 5 sites (Table 5).

Table 5. Summary of fDOC response at excitation wavelength 300 nm and emission at wavelength 350 nm (λ_{ex}=300, λ_{em}=350), compared with nutrient concentrations, in collected water samples

Site	Fluorescence units	Nitrogen (mg/L)		Phosphorus (mg/L)	
		Total	NO_x	Total	PO_4^{3-}
Police Barracks (Burke River)	34	0.52±0.03	0.02±0.01	<LOR[a]	<LOR
Boulia (Burke River)	18	0.38±0.46	0.31±0.42	<LOR	0.05
Georgina (Georgina River)	62	0.46±0.12	0.11±0.03	<LOR	0.01±0.001
Bedourie (Georgina)	53	2.61±1.91	3.58±0.41	<LOR	0.01
Cluny (King Creek)	47	0.46±0.3	0.03±0.02	<LOR	0.01±0.003
Glengyle (Eyre Creek)	74	1.36±0.03	1.22±0.12	0.22±0.19	0.07±0.01
Oondoroo (Mills Creek)	18	0.56±0.08	0.04±0.02	0.04±0.02	0.02±0.001
Old Cork (Diamantina River)	272	0.29±0.33	0.11±0.09	<LOR	0.01
Diamantina NP (Diamantina River)	166	1.2±0.54	0.89±0.03	<LOR	0.07±0.01
Davenport Downs (Diamantina River)	155	0.43±0.11	0.40±0.13	0.09±0.02	0.08±0.02
Brumby Waterhole (Diamantina River)	53	0.61±0.5	0.43±0.3	0.45±0.01	0.19±0.08
Birdsville (Diamantina River)	41	0.83±0.38	0.62±0.62	0.22±0.01	0.06±0.03
Pandie Pandie s(Diamantina River)	117	0.94±0.09	0.53±0.12	0.28±0.01	0.16±0.01
Clifton Hills (Diamantina River)	199	1.41±0.13	1.17±0.06	0.41±0.05	0.24±0.01

[a]Limit of reporting

Discussion

Water chemistry

The elevated nitrogen and phosphorus concentrations, along with the biologically utilisable NO_x and PO_4^{3-} species, in water are consistent with previous water quality data collected for LEB. Elevated nutrient concentrations, especially in the case of nitrogen and phosphorus, are often implicated in eutrophic conditions where high nutrient concentrations are associated with high primary production and severely limited dissolved oxygen concentrations. Dissolved oxygen concentrations, however, were found to be around saturation levels, indicating all water bodies were well oxygenated. Furthermore, chlorophyll *a* concentrations are consistent with a moderately productive system.

At most sites, turbidity was similarly elevated in accordance with previous data (Table 2) and the elevated turbidity may explain in part the lower than expected chlorophyll *a* concentrations measured at all sites. There was not a direct relationship between turbidity and chlorophyll *a*, however, with higher turbidity occurring at the southern range of sampling and chlorophyll *a* concentrations not showing any such geographic relationship (Figures 4 and 5). Chlorophyll *a* concentrations are lower in comparison with a survey conducted in spring 2012 by the SA EPA (Table 2), although the study did not include turbidity data for comparison. Despite exceeding the default trigger values for turbidity in low rainfall areas of southern Australia, high turbidity is considered to be a feature of water bodies within the LEB due to relatively high concentrations of suspended clays (Silcock 2009).

The relatively high degree of oxygenation and low chlorophyll *a* concentrations, along with other measured water quality data (such as pH and electrical conductivity), suggest that the water quality was generally good at the sampled sites. This is despite the elevated nitrogen, phosphorus and turbidity. Further assessment of biological productivity in the water bodies (such as fish and invertebrate surveys) would be required to confirm whether the measured water chemistry parameters are consistent with a healthy system. A previous study assessing fish population and diversity at a number of LEB sites, including Davenport Downs, Old Cork and Diamantina Lakes (within Diamantina National Park) also collected water quality data, such as total phosphorus, electrical conductivity and dissolved oxygen (Long and Humphery 1995). The study by Long and Humphrey (1995) showed reasonable to good levels of fish abundance and diversity with slightly higher total phosphorus concentrations and considerably lower dissolved oxygen concentrations, compared with the present study. High levels of turbidity (measured with a Secchi disk) and total Kjeldahl nitrogen (TKN) were also noted by Long and Humphrey and this would suggest that the water chemistry parameters measured in the present study would also be supportive of fish populations. Another study also rated a good habitat condition for macroinvertebrates in the majority of 30 sites sampled in eastern LEB catchments with similarly elevated N, P and turbidity values and low EC (Choy et al. 2002).

Although the concentration of Al in water samples was elevated above the ANZECC/ARMCANZ (2000) trigger value at 10 of the 14 sites, this needs to be considered in light of the effects of water chemistry on Al toxicity. Al is highly abundant in the environment and is generally present as oxide or aluminosilicate species but can also be present as other organic or inorganic species. Between pH values of 5 and 8, Al is generally present as insoluble polymeric or hydroxy species, while it is generally in its most toxic form (Al III) below pH 5 (Driscoll and Schecher 1990). Speciation is taken into account within water quality guidelines, with differentiation made between concentrations of Al either greater than or less than pH 6.5 (ANZECC/ARMCANZ 2000). Although all of the water samples had pH >6.5, more comprehensive analytical techniques would be necessary to assign speciation to Al present in the water samples and contribute to understanding its potential toxicological risks within the system.

Sediment chemistry

With background information largely unavailable for sediments in the LEB, with respect to historical data and sediment quality guidelines, it is difficult to draw any conclusions on the sediment quality of the collected samples. The collection of sediments in this monitoring campaign therefore represents an important contribution to the understanding of their physicochemical properties within the LEB. Sediments have an important influence on water quality, are an ultimate repository of many chemicals (including contaminants) and can act as a source or sink of such chemicals to biota, including the aquatic food chain (ANZECC/ARMCANZ 2000, Simpson et al. 2005).

One notable finding related to the organic carbon of the collected sediments being less than 1% at all sites (Appendix 6). Organic carbon can have an important influence on the ability of biological organisms to access a range of chemicals in solution, including nutrients and trace elements, although organic carbon concentrations of <1% are likely to have a negligible effect on their bioavailability (ANZECC/ARMCANZ 2000). The finding on the measured concentrations of arsenic (As) exceeding lower interim sediment quality guideline trigger values (ANZECC/ARMCANZ 2000) at 9 of the 14 sites is noteworthy (Appendix 6). As with nutrients (such as N and P) and other trace elements (such as Al), As can be present as a number of different species, each with variable accessibility to biological organisms and inherent toxicities. Inorganic As can be in the form of As(III) or As(IV), which are considerably more toxic than the large variety of organic As species that may exist in the environment (Jonnalagadda and Rao 1993). Assessment of the dominant As species present in the sediment samples, and their potential toxicological implications, requires more comprehensive analytical techniques. This is also pertinent to elements such as Fe and Al, found at high levels in the sediments, which can exist as different species in the environment impacting on their availability and toxicity to organisms (Borch et al. 2010). For all of these elements (Al, As and Fe) the concentrations of Al and Fe in solution (Figure A10) and As <LOR (0.05 mg/L) were comparatively very low, relative to their sediment concentrations (Figures A18 and A19). This would indicate that the ability of these three elements to mobilise into solution from the sediments is also very low, suggesting their sediment concentrations are unlikely to have an impact on toxicity. This is also consistent with these three elements being components of the natural soil and sediment mineralogy, as opposed to being contaminants, although this should be confirmed with a mineralogical assessment of the soils and sediments.

Corresponding soil and manure samples had nutrient and trace element profiles similar to that measured in the sediment (Appendix 7). For example, levels of Al, Fe and Zn were respectively in a similar range in sediment, soil and manure samples. The concentration of C, N, P and As, however, were more closely related in the soil and sediment samples compared with the manure samples, although the composition of nutrient species (NO_x, NH_4^+ and PO_4^{2-}) was more variable between soil and sediment.

Monitoring potential impacts on water quality

The assessment of fDOC and hormones in collected samples as a means of source identification did not clearly define potential sources for elevated nutrient levels within the monitored catchment. Hormones were detected in a limited number of samples and there was no consistency in the hormones that were detected in terms of the relative concentrations of estrone and androsterone measured respectively in sediment and water. At the time of sampling, water levels were low and few cattle were noted, if at all, where samples were collected. Evidence of cattle, such as tracks and dried manure, were apparent at all sites but it was not possible to define when the cattle were present at the sampling site. Density of tracks and manure around

waterholes did not indicate a high number of cattle visiting the sites around the time of sampling. A number of cattle were present at some of the sites during sampling but these generally numbered less than half a dozen for each sighting (Appendix 1). The greatest numbers of cattle in relation to proximity to waterholes were observed in the Diamantina National Park, where dozens of cattle were seen within a few kilometres of the sampling site (Diamantina NP). Low levels of the estrogenic hormone estrone were detected in sediments at Diamantina NP but not in the water column. On the other hand, the androgenic hormone androsterone was detected at a number of sites in the water column but not in sediment samples and not at Diamantina NP.

The detection of estrogenic and androgenic hormones in the environment is not only dependent on how they were excreted (e.g. male vs female) but also on the environmental processes that may have occurred following excretion of the hormone (Kolodziej and Sedlak 2007; Ying et al. 2008). Ratios of different hormones has been previously used to assess sources of livestock contamination in water (Furtula et al. 2012), although these hormones were either not within available analytical capabilities or were below detectable limits. The presence of certain hormones in isolation from others therefore makes it difficult to draw any conclusions relating to potential impacts from cattle from hormone analysis alone.

With respect to fDOC, the spectra obtained at λ_{ex}=300 nm, λ_{em}=350 nm, relating to tryptophan-like DOC, is used to monitor sewage-derived water since tryptophan-like DOC is derived from proteins, indicative of microbial activity. Growth of marine algae has also been shown to increase the intensity of protein-derived DOC fluorescence (Stedmon and Markager 2005). This is in contrast to fulvic and humic-like DOC, which is derived from breakdown of plant-based material (Henderson et al. 2009). Strong, indirect correlations between tryptophan-like DOC and biological oxygen demand (BOD), PO_4^{3-}, NO_3^-, total Kjeldahl nitrogen (TKN) and NH_3 have been demonstrated, further highlighting the usefulness of fDOC to monitor impacted waters (Henderson et al. 2009). With an extremely low population density in the LEB, however, it is unlikely that sewage impacts would be found. Tryptophan-like fDOC is therefore more likely to be derived from activity of cattle within the area and fluorescence intensity of tryptophan-like fDOC (λ_{ex}=275 nm, λ_{em}=350 nm) in cattle slurry collected from dairy farms be up to three times greater than reference river water (Baker 2002). The sites with the highest tryptophan-like fDOC were on the Diamantina River at Old Cork, the Diamantina NP, Davenport Downs, Pandie Pandie and Clifton Hills, with fluorescence units measurements >100 (Table 5). As a comparison with the fluorescence values obtained, purified sewage used for recycling purposes measured under the same analytical conditions usually has fluorescence values >100 (Hambly et al. 2010), while ultrapure water generated in the laboratory had a value of <1. The elevated concentrations at the sites, however, did not necessarily correspond with elevated nutrient concentrations in the water samples. For example, Old Cork had the highest fDOC concentrations but also had some of the lowest NO_3^-/NO_2^- and PO_4^{3-} values (Table 5). Conversely, Brumby Waterhole had relatively low fDOC levels but had amongst the highest PO_4^{2-} and total P values (Table 5). Water bodies within the LEB have been found to support ecologically-critical algal populations, which may have also contributed to the fDOC signal measured in the water samples. Chlorophyll *a* concentrations measured in the water samples were not able to be related to the fDOC signal intensity. For example, the highest chlorophyll A concentrations were measured at Old Cork and Brumby Waterhole (Figure 4), while the fDOC at these sites was markedly different (Table 5).

Despite these two lines of evidence to assess potential impacts from grazing activity, there was no apparent consistency between the measurements. The low numbers of cattle observed at the sampling sites would support, for example, the non-detectable to low concentrations of hormones in water and sediment samples. Without a consistent input of hormones into these systems, they would be expected to be reasonably labile to degradation through microbial activity (Writer et al. 2011). It is difficult to rule out the potential for the elevated nutrient concentrations being derived from livestock, based on the low concentrations measured in soils and sediments and the high concentrations measured in the manure (Appendix 7). Attributing the elevated nutrient concentrations to livestock is equally difficult, since few

cattle, cattle tracks and manure at all of the sampling sites did not indicate recently high numbers of visitations.

Apart from livestock, other potential sources of nutrients could be the surrounding riparian vegetation and soil. The riparian zone surrounding all the waterholes was observed to be generally productive and included stands of *Eucalyptus* spp. (probably *Eucalyptus coolabah*), which (along with other riparian vegetation) can play a role in trapping nutrients in the riparian zone (Silcock 2009). The profiles of nutrient and trace element concentrations within the collected soil and sediments were similar, which may indicate the origin of the sediment could indeed be related to soil inputs. Despite the elevated levels of nutrients in the water column, the concentrations of nutrients such as NO_3^- within the soil surrounding the waterholes was at the lower range of values that have been measured in other arid regions in Australia (e.g. by Charley and McGarity 1964) and globally (Graham et al. 2008). It has been suggested that inputs of sediments from soils into LEB waterways is largely driven by the major flooding events that can occur in the region (Silcock 2009). During periods of no flow, continuous mixing and evaporation of shallow waterbodies through wind action and inputs of soil and riparian vegetation into waterholes are all likely to contribute to elevated nutrient concentrations in the waterholes (Crawford and Gosz 1982; McTainsh and Strong 2007). Evaporation within the LEB is substantial and with rates of more than 2 m/yr being recorded in the Cooper Creek it is likely to dominate the hydrology of waterholes (Hamilton et al. 2007). Nutrient concentrations in waterholes during periods of no flow in the LEB region have been previously shown to be greater than during flood or flowing conditions, with mean total N and P concentrations being nearly 3 times and 2 times greater during periods of no-flow compared with flow (Sheldon and Fellows 2010). With similar increases also seen in mean EC and TDS, this supports the idea of such concentrating effects on water quality parameters in waterholes.

Along with these natural processes, access by livestock could exacerbate these effects but clearly more research is required to confirm the extent of relative contributions. Siltation, which can increase loss of water from waterholes and enhance such concentrating effects, can be enhanced by clearance of vegetation from riparian zones. Although siltation largely occurs due to natural processes, grazing by livestock and other introduced species can increase the impact of this problem through loss of stabilising riverbank vegetation (Silcock 2009).

From the limited historical data available, there is reasonably good agreement between nutrient concentrations measured in the present campaign and in previous campaigns (Table 2). This does not necessarily imply that the nutrients are at a background level because of limitations relating to the timescale of data for comparison; the earliest available data are from the 1970s, while considerable livestock activity has been present in the LEB for around 140 years (Silcock 2009). Other literature suggests that elevated nutrient concentrations can be found in arid regions due to inputs from organisms adapted to this climate zone, including microbial “crusts” on soils and through nitrogen-fixing leguminous plants (Crawford and Gosz 1982). Also, comparable water nutrient concentrations reported in other studies incorporating biological surveys have been associated with good biological condition assessments, suggesting that these apparently high nutrient concentrations may not be a significant stressor on biological communities in the surveyed waterholes (Fellows et al. 2009; Fellows et al. 2007; Long and Humphery 1995).

Source tracking – other markers to identify contaminant sources

One of the objectives of this project was to suggest tracers or markers that could be used to identify contaminant sources in future monitoring programs in the LEB. Therefore, a literature review was conducted of various markers that have been used for tracking sources of contamination impacting freshwater systems. The literature review revealed a myriad of markers that have been used with varying degree of success. These included isotopic elemental markers (e.g. N, O, B, U), fDOC especially relating to protein-like

compounds with fluorescent properties, sewage-associated trace organic compounds (e.g. pharmaceuticals, hormones, artificial sweeteners), microbial source tracking (MST) to discriminate between human and non-human sources and also to track specific animal sources and molecular organic proxies of phytoplankton. The detailed literature review of different classes of markers has been presented in Appendix 9. We also evaluated the strengths and weaknesses of these markers, especially in the context of dominant land uses in the LEB, and considered their suitability with respect to conditions in LEB. The markers that were identified to be not suitable or potentially useful are discussed below.

Unsuitable tracers for LEB

While a range of tracers, such as those associated with sewage (e.g. artificial) have been found to be specific and sensitive in sewage-impacted environments, these are largely unsuitable for the LEB, mainly because human sewage is not expected to a major source of nutrients and other contaminants in the LEB. Examples of such tracers include artificial sweeteners, pharmaceuticals, medical-imaging contrast media and stimulants. There are many arid regions globally that are highly populated (e.g. China, North America, Middle East) where the receiving environments are expected to be impacted from sewage and such markers would be particularly useful in this context.

Isotopic tracers such as $\delta^{11}B$, may similarly not be of any use for the above reasons, as it is a marker primarily associated with wastewater discharges (Cary et al. 2013). The isotopic ratio of $^{234}U/^{238}U$ would also not be relevant as it is associated with inorganic fertilisers from certain sources (e.g. Florida). Agriculture has a minimal presence in the LEB, so inputs of fertiliser are likely to be minimal, as well as background levels of U in LEB being relatively high and making distinguishing this tracer difficult. Similarly the dual isotopic approach based on N and O that can be useful in differentiating the sewage-derived nutrients from inorganic fertiliser sources, are not appropriate for the LEB.

Suitable/potentially suitable

With around 80% of the basin area under livestock grazing, monitoring chemical signals from grazing animals are of interest. In recent years, genetic biomarkers associated with particular animal faeces have become attractive tools of microbial source tracking (MST). An inter-laboratory study involving 27 different laboratories and 41 MST methods Boehm et al. (2013) identified a range of specific and sensitive assays covering human, and various animal-specific sources including cows, pigs, chicken, horse and other animals. The top performing assays were for Humans - HF 183; for ruminants - CF 1 and Rum2Bac; for cows – CowM2 and Cow M3; for pigs – pigmtDNA; for horse – HoF597 (Boehm et al. 2013). Microbial source trackers are emerging as sensitive and specific markers and are highly relevant to the land use in the LEB. These include specific hormonal markers such as alpha estradiol or degradation products, or the genetic markers such as CowM2 and CowM3. Fluorescent DOC is a relatively rapid and cheap option. A limited study in this Goyder project has indicated that fDOC is able to pick up signals from certain sites, which may be indicative of animal activities. Therefore a combination of specific genetic markers together with fDOC may be particularly useful. Multiple tracers are often needed to confirm the contamination sources.

Source tracking in the present study was related to a number of estrogenic and androgenic hormones but this could be expanded to include a number of other related cholesterol-based hormones and steroids. For example, a study in California found a number of steroid hormones similar to those screened for the in the

present study, along with a number of others including progesterone and medroxyprogesterone (Kolodziej and Sedlak 2007).

Study on the contaminant source trackers in Georgina-Diamantina system

Considering the land use within the LEB being predominantly cattle grazing, two markers were used to assess the potential influence that cattle could have on the waterbodies. These were hormones and fDOC. Due to low population density, previously used tracers of human activity relating to sewage discharges (such as pharmaceuticals and personal care products) and agricultural activities (such as pesticides) were not considered.

Hormones were generally not detectable at the majority of sites, however, an androgenic hormone, androsterone, was found in the water column at six sites. Another estrogenic hormone, estrone, was found in sediments, were it was present at seven sites. While hormones were detected in a limited number of samples, there was no consistency in terms of the relative concentrations of estrone and androsterone measured respectively in sediment and water. The excitation-emission spectra (λ_{ex}=300, λ_{em}=350) of fDOC were elevated at some sites, although these may be indicative of not only external inputs of protein-like fDOC but also of algae present in the waterbodies. Evidence of cattle, such as tracks and dried manure, were apparent at all sites but it was not possible to define when the cattle were present at the sampling site. The greatest numbers of cattle in relation to proximity to waterholes were observed in the Diamantina National Park. Here low levels of the estrogenic hormone estrone were detected in sediments but not in the water column, whereas the androgenic hormone androsterone was detected in the water column but not in sediment samples. Estrone is a metabolic product of the androgenic hormone androstenedione and of the estrogenic hormone estradiol. The occasional presence of certain hormones did indicate livestock link but was not enough to draw any conclusions relating to livestock as a source of pollution.

Recommendations for future monitoring programs

As noted previously, the sampling techniques and analytical methodologies applied to collected samples are likely to be inconsistent in the present study compared with historical campaigns. This inconsistency makes it difficult to make conclusions on long-term data trends since comparisons between sampling campaigns often, at best, require qualification of collated data or, in the worst case, make comparison impossible. Historical data collected from scientific literature generally gave the most detailed descriptions of sampling collection and analytical methodology, although this was generally more explicit in publications specifically targeting water quality (Sheldon and Fellows 2010). The SA EPA database specified analytical procedures for each analyte, where laboratory-based analysis was undertaken by an accredited analytical service.

Inclusion of sampling methodology is also important since all stages of field collection and sample preparation may introduce artefacts that can influence the final value obtained for a parameter. For example, variables that may influence the results obtained for water quality parameters include position and depth of collection within the waterbody, material used for collection containers, filtration or homogenisation of samples, depth or position of sampling, amongst a myriad of other potential sampling artefacts (ANZECC/ARMCANZ 2000b). Within LEB, for example, Long and Humphery (1995) showed that depth of sampling has an effect on DO and temperature despite the relatively shallow waterbodies, while Costelloe et al. (2005) demonstrated that diversity and abundance of algae populations around the shoreline of waterbodies was greater than in mid-stream collections.

Collection of sediments is fraught with more sampling artefacts since sediments are often highly heterogeneous and more susceptible to physicochemical changes following collection (Simpson et al. 2005). For example, mixing of sediments for homogeneity is necessary for providing a reproducible sample for analysis but it can effectively dilute any chemicals unevenly distributed throughout the sediment. Collection of sediments will expose them to oxygen, which can also have an impact on parameters such as pH and redox potential, which can affect metal speciation (Simpson et al. 2005). Effective preservation of sediment samples can also prove to be more difficult than water samples, with a number of parameters changing relatively soon after collection. Although total trace element concentrations are unlikely to change, their speciation can change fairly rapidly, while ongoing microbial activity can also cause changes in levels of analytes including ammonia and organic compounds, such as hormones (Simpson et al. 2005). The location of sediment collection sites within the waterbody is important, as well as the depth of sampling within the sediment column. The majority of biological activity occurs within the top 100 mm of sediments, although this is dependent on species present within the waterbody, while depositional depth of sediments also means the top layers of sediment is more representative of recent deposition (Simpson et al. 2005). In a catchment with such extreme variability in flows, this can make judgement of sampling depth more difficult. Since collection of sediments in the present study occurred at the end of long dry period, an approximate 50 mm depth of collection was considered suitable, although future campaigns may need to consider the most appropriate collection strategy based on the recent flow history. All of these factors can make inclusion of sediment collection and analysis less attractive in terms of additional labour and resources required. Furthermore, there still remains considerably more scientific uncertainty relating to sediment quality compared with water quality and it can be difficult to draw conclusions for some parameters, especially where more detailed analysis may be required (e.g. speciation of As). Sediments are an integral component of water bodies, however, and being a repository of many contaminants, or indicators of contaminants, makes their inclusion important in any condition assessments of waterbodies. As outlined above, analysis of hormones, trace elements or diatoms can be more sensitive in sediments due to their accumulative properties and it is especially critical where these impacts are considered to be currently minimal and against which any future impacts can be measured.

One major challenge of sampling in arid remote locations such as the LEB is appropriate sample preservation and storage. It is generally recommended to keep them refrigerated rather than frozen (Simpson et al. 2005). This also applies to an analytes such as fDOC, where freezing can change its characteristics (Baker et al. 2003), although optimal preservation of nutrients requires that samples be frozen (Avanzino and Kennedy 1993). This is also a challenge in warm climates where great distances need to be covered and adds considerably to logistical requirements, where samples need to be split and stored separately where space is at a premium. This leads to the fact that accounting for samples through record information and quality assurance/quality control (QA/QC) protocols are in place (ANZECC/ARMCANZ 2000). One QA/QC procedure included using field blanks (ultrapure water taken into the field in appropriate sample containers) for all analytes to assess potential for contamination and/or ability of analytical equipment to account for background measurements. For a procedure such as chlorophyll *a* sampling and analysis, which is highly susceptible to degradation and sample preparation artefacts (Latasa et al. 2001; Simon and Helliwell 1998), it would be desirable to include more rigorous procedures, such as spiking field blanks with standard concentrations of chlorophyll *a* to assess its stability in the field. Regular and appropriate calibration of field equipment and laboratory-based analytical equipment. Making sampling and analytical information available can enable greater understanding of values obtained for water and sediment quality parameters, which will give greater weight to conclusions relating to their values. It would also allow greater consistency with or refinement of future water and sediment quality sampling programs.

Physicochemical measurements of waterbodies to enable effective condition assessments need to be considered within the context of corresponding biological monitoring campaigns. Biological sampling and analysis is considerably laborious and inclusion of a full suite of water and sediment quality parameters is not

always practical or possible with available resources. A minimum of physicochemical parameters should be included in any sampling campaign, which in the case of LEB systems should include pH, EC, DO, turbidity and a number of relevant nutrient measurements (e.g. total N and NO_x). Consistent sampling and analytical methodology should also be considered to make comparison with biological indices are more meaningful. For example, nitrogen can be measured converting all N in a sample to N_2 (thermal conductivity detection) or through TKN. If TKN is used, further analysis of water for NO_3^-/NO_2^- needs to be undertaken to account for total N, since the TKN method cannot convert such N-containing groups (as well as some forms of organic N) into a measurable value (USEPA 1993). More extensive analysis of waterbodies, including larger suites of analytes, sediment sampling and inclusion of source tracking analytes, require more technical expertise and resources and, while critical in the assessment of conditions within the catchment, can be done less frequently.

Finally, although there was good agreement with previous sampling campaigns, the water quality results obtained from the present sampling campaign should be treated with caution, since they represent a single temporal collection in a highly variable system. On the other hand, the low water levels during the sampling are likely to represent a "worst-case scenario", in terms of nutrient concentrations (Sheldon and Fellows 2010). Indeed, Sheldon and Fellows (2010) argue that water quality trigger values should be based on periods when flow occurs to reduce the variability in baseline values and make the trigger values more meaningful. Alternatively, it has been suggested that trigger value ranges may be more appropriate in areas of high variability (Hart et al. 1999). Based on the consistent exceedance of a number of ANZECC trigger values for low rainfall regions of Australia, including nitrogen and phosphorus concentrations in water and turbidity, it seems that there is a good case for reviewing the existing water quality guidelines in this region. This would also enable greater confidence in the relevance of water chemistry data used in integrated condition assessments of waterbodies in the LEB.

Conclusions

The main conclusions of this study were:

- Water quality data for the LEB were available for the last four decades, although the data had generally been collected sporadically, at relatively large spatial intervals and focussed on comparatively few measurements, especially nutrient concentrations, turbidity, pH and electrical conductivity. Sites within the Cooper Creek catchment had the greatest amount of data. Collated water quality data generally showed elevated nutrient and turbidity values, with respect to the national default water quality guidelines, although pH, dissolved oxygen and electrical conductivity were within guideline values. No sediment quality data were found.
- A one-off sampling campaign in spring 2014 in the Diamantina-Georgina River catchment found water quality parameters were generally consistent with collated historical data and were also found to exceed default ANZECC/ARMCANZ water and sediment quality guideline trigger values for nutrients (N and P species), trace elements (Al and As) and turbidity at the majority of sites. Sediment quality parameters measured during this campaign will make an important contribution to existing knowledge gaps relating to sediments in LEB waterbodies.
- The significance of water quality parameters exceeding national guideline values is difficult to evaluate in the absence of additional chemical assessments (e.g. chemical speciation of trace elements) or of concurrent biological surveys in the sampled waterholes. The consistency of the water quality parameters measured during this campaign with historical water quality data, especially when collected alongside biological surveys, suggest that these elevated levels may be a natural feature of the LEB and may not be of concern. If this is the case, then the available water

quality parameters may be useful as comparisons with future water (and sediment) quality monitoring to ensure these “baseline” levels do not change over time.

- Monitoring of water and sediment quality parameters should have minimum standards applied to them, such as following and documenting sampling and analytical protocols, to ensure measurements made during monitoring campaigns are consistent and comparable over long timescales.
- A number of parameters were identified as being suitable for tracking sources of potential pollution in LEB, based on livestock grazing being one of the most widespread land uses. Hormones and the fluorescence signal of dissolved organic carbon (fDOC) were not able to definitively link livestock grazing with elevated nutrient inputs into waterways. Furthermore, nutrient and trace element profiles of soils surrounding the waterholes suggest that soil inputs would have an important role in sediment composition.

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Appendices

Appendix 1. Overview of sampling sites

Table A 1. Overview of sampling sites

Site	Coordinates	Water		Sediment	Comments	
		Level below top of bank	Description		Potential impacts	General
Police Barracks (Burke River)	S22.71926 E140.03383	~5m	Murky brown/ green; low turbidity, easily filtered. Very small pool of water	Sandy/ gravelly full depth;organic detritus from overhanging trees	~6 cattle present; tracks and dry manure in river bed. ~200m from picnic area.	Light/moderate SE/E winds Very flat, increasingly forested with knee high (to grazed) grass. Red gibber; less forested north of Boulia; close to Bourke River good tree/ grass coverage, eucalypts to 10m Red sandy clay, rocky near river
Boulia (Burke River)	S23.41559	~4-5m	Turbid, grey/green colour, easily	Fine clay (grey/brown) with anoxic	Tracks, fresh manure on	Moderate NE wind.

	E139.66887		filterable	grey/black sediment ~40mm depth; dark green algal crust	opposite bank Campfires + fresh (dog?) faeces Small to large (10-500mm) algal mats (dark green/grey/black) floating	More permanent hills but generally flat countryside, grasslands dominant heading north Low trees (e.g. eucalypt, waddi) more dominant
Georgina (Georgina River)	S24.10070 E139.56407	~3m	Reasonably turbid, clay (brown/yellow) colour with algae; Easily filterable	Fine clayey sediment; reddish brown crust (0-5mm), grey below. No algae	~12 cattle drinking; fresh manure. 4WD track to water hole. Small clumps of dark green algal floating on surface	Light E/NE breeze. Flat dry clay floodplain surrounded by yellow sand dunes More vegetation coverage closer to waterway as heading north from Bedourie
Bedourie (Georgina)	S24.36787 E139.46935	~4m	Reasonably turbid; grey green colour	Gravel/coarse sand (top 10mm); sandy clay (grey) below; topped with algal crust	No livestock present; cattle tracks; some dried manure (fresh inside crust).	Light SE breeze Flat sandy country, generally few shrubs, trees although some

					Large clumps of algae floating on surface. Township ~500m north	areas of darker clay.
Cluny (King Creek)	S24.53157 E139.56467	~3m	Reasonably turbid	Sandy grey sediment with organic detritus, top layer (0-10mm) oxidised crust	No livestock present; cattle tracks; some dried manure. Large covering of dead tree leaves at end of pool	Light to moderate E/SE breeze Country immediately north, very flat, sandy, red dune ridges
Glengyle (Eyre Creek)	S24.83410 E139.62277	~3m	Reasonably turbid, easily filterable	Grey sediment uniform over 50mm depth. Algal crust on surface; fine to medium grains	3 cattle sited, some dried tracks/manure Stopover point for tourists (campfires/ caravans) Some algal growth on shoreline	Fresh SE wind. Surrounding countryside: Clay, waist high grass close to creek Sandy further inland
Oondoroo (Mills Creek)	S22.17423 E143.16597	~3-4m	Murky brown, reasonably turbid	Medium brown/grey sediment with algal crust growing on top	No cattle evident, tracks and manure (dry) around edges. Clumps of green	Light winds. Surrounding land very dry little grass, small eucalypts/

					algae (dark green) floating and growing on edge of waterhole. Homestead ~1km away	acacias
Old Cork (Diamantina River)	S22.91718 E141.89355	~3-4m	Murky brown, turbid	Brown sand, very fine,	No cattle evident tracks/ manure. Campfires ~200m upstream	Light SW wind. Flat, very dry surroundings, grassy within 1km river, extensive small (to 3m) eucalypts Brown clay/ fine sand
Diamantina NP (Diamantina River)	S23.72352 E141.11261	~6m	Very turbid, brown clay colour, slow to filter	Clay (brown/yellow) very fine	Cattle tracks along bank and manure (dry); dozens of cattle sited in national park in channels. Ranger station ~5km away	Light to moderate S/SE (strong previous night). ~200m from flow station.
Davenport Downs (Diamantina River)	S24.15573 E141.10057	~2m	Very turbid; brown/yellow colour (water	Silty clay (brown); anoxic smell	~6 cattle present, tracks. ~500m from	Moderate SE/E wind. Around station

			birds present greatly increased turbidity)		homestead, campfire present	very flat, grass very low to none. Eucalypts only on bank.
Brumby Waterhole (Diamantina River)	S25.65426 E139.83675	~2m	Very turbid, yellow/brown clay colour	High clay/water content	No livestock present; cattle tracks at top of bank; some dried manure.	Fresh SE/E wind Long, wide waterhole
Birdsville (Diamantina River)	S25.90824 E139.36662	~4m	Very turbid, yellow/brown clay colour	Fine clay top 20mm, below which grey clay sediment; high water content	No livestock present; cattle tracks ~1m above water level; some dried manure. Some algal growth on shoreline	Light to moderate SE breeze EPA monitoring station
Pandie Pandie (Diamantina River)	S26.12837 E139.38640	~10m	Very turbid, yellow/brown clay colour, choppy from wind	Grey fine clay with algal mat on top	No livestock present; cattle tracks and dry manure. Homestead ~200m away	Moderate to fresh N/NE. High dunes, sandy surrounds; generally low bushes, little to no grass; very dry Low eucalypts all the way to dunes/

						homestead
Clifton Hills (Diamantina River)	S26.53419 E139.45035	~10m	Very turbid, yellow/brown clay colour, calm surface	Light brown/yellow 0.5mm with fine grey clay below, some algal growth on surface	No cattle/ tracks evident Outstation ~30m from edge of bank	Light N wind. Just south of Birdsville dunes until outstation. Flat clay/sand along flood plain. Waist to head high lignum main vegetation, little grass. ~dozen cattle spotted between Pandie and Clifton (only ones spotted in SA)

Appendix 2. Sampling methodology

Water quality data – field collection

Surface water samples for laboratory analysis were collected by immersion of a pre-rinsed 7 L 'garden spray' container in the water body. All water samples were filtered using positive pressure through a 47 mm GFA 1.6 µm prefilter and 47 mm 0.45 µm MCE filter using a polypropylene 47 mm filter holder. Surface water samples were filtered into new 50 mL polypropylene tubes without headspace. One replicate sample was acidified in the field with 0.5 mL concentrated nitric acid (Merck UHPC grade) for the preservation of sample for metal and metalloid analysis.

Samples for chlorophyll *a* analysis had approximately 50 mL of water per replicate passed through a 0.3 µm glass fibre filter using positive pressure. The filter paper was then placed in a 50 mL polypropylene tube, containing an excess (~2 g) $MgCO_3$ and immediately placed in the dark. All collected samples were immediately placed in an ice box containing ice or in a portable refrigerator/freezer, with sub-samples for nutrient analysis placed within the freezer compartment.

Water samples for hormone analysis were collected in 500 mL amber glass bottles, with 0.25 mL concentrated H_2SO_4 added for sample preservation. Sample bottles were also placed in ice boxes on ice.

Sediment sampling

Replicated 0-50 mm samples were collected with a spade, ensuring minimal disturbance to surrounding sediments, with an average of four sub-samples combined into a homogenized bulk sample in a stainless steel mixing bowl. Mixed sediment was transferred to acid-washed and baked 1L glass jars with air excluded to minimise oxidation. Redox potential (Eh) and pH readings were taken at sampling using a TPS WP81 meter with Ionode IJ44 pH and IJ64 Eh electrodes. Meter and probe calibrations were checked against Zobell's solution for Eh and a two-point calibration (pH 4 and 7) for pH.

Soil samples were collected from the top of the embankment of waterbodies, and collected from a maximum depth of 50 mm into 50 mL polypropylene tubes, avoiding inclusion of any vegetative matter. A number of manure samples were randomly sampled from around the soil collection area (when available) and each sample had the outer crust removed before being pooled in. Sediment, soil and manure samples were placed on ice in ice boxes after sampling.

Upon the return from the field, all samples were immediately transferred to either 4 or -18^{o}C temperature-controlled rooms (depending on analyte) prior to analysis. Filter papers for chlorophyll *a* analysis were stored in -80^{o}C freezers until analysis.

Appendix 3. Analytical methodology

Field analysis of water samples

Water quality data were logged in situ of sample collection using a YSI 556 multiprobe sonde with data collected for temperature, dissolved oxygen, ORP (redox potential), pH, total dissolved solids (TDS), salinity and conductivity (EC). Turbidity was measured using a TPS WP88 turbidity meter in situ after calibration on a 900 NTU standard. The YSI sonde was pre-calibrated before sampling at regular intervals using relevant standards as per instrument protocol. Dissolved oxygen as calibrated as percent saturation in air. ORP was calibrated on Zobells solution at 20^{o}C. SEC calibrated at 10mS/cm for saline samples and 2.76 mS/cm for freshwater samples. The pH meter was calibrated at 7 and 10 with NIST certified buffers, this calibration was in range with the surface water pH readings at all sites.

Field alkalinity was measured using a HACH Alkalinity test kit Model AL-DT to measure alkalinity in surface waters by titration with a standard sulphuric acid solution to a colormetric end point. A 100mL aliquot of water is added to a reaction flask with a colour indicator sachet (phenolphthalein) dissolved into the sample. The standard acid is added dropwise until the pale pink endpoint is reached to determine alkalinity as mg/L calcium carbonate.

Nutrients

All nutrients were analysed by the CSIRO Analytical Services Unit (Waite Campus, SA).

Total carbon and nitrogen were determined by high temperature combustion in an atmosphere of oxygen using a Leco TruMAC. Carbon was converted to CO_2 and determined by infrared detection. Nitrogen was determined as N_2 by thermal conductivity detection following the method of Matejovic (1997).

Inorganic C was determined following Rayment and Lyons (2011a) and Sherrod et al (2002). The sample was reacted with acid in a sealed container and measuring the pressure increase. Sufficient finely ground sample to contain no more than 0.8 g $CaCO_3$ equivalent was weighed into a 250 mL glass bottle, a tube containing 8 mL 3 M HCl and 3% ferrous chloride added and the bottle sealed. The contents were mixed intermittently during a 1 hour period and the pressure in the bottle measured by piercing the septum with a needle attached to a pressure transducer

Inorganic nitrogen was determined by segmented flow colorimetry following extraction using 2M KCl. Nitrate was dialysed then reduced to nitrite by Cd reduction and the resultant nitrite reacted with N-1-naphthylethylenediamine dihydrochloride (NEDD) with sulfanilamide (Rayment and Lyons 2011). NH_4^+, determined following a modified ISO method (ISO 1997), was separated from interferences by gas diffusion and determined after reaction with sodium salicylate and dichloroisocyanurate (DCIC).

Extractable phosphorus was determined by segmented flow colorimetry following Colwell extraction using 0.5M $NaHCO_3$ at pH 8.5. (Rayment and Lyons 2011b).

Fluoride, bromide, sulfate [APHA method 4110]. These common anions are determined by ion chromatography using a Dionex ICS-2500 system with 2mm AS16 anion separation column and hydroxide eluent generated on line followed by conductivity detection after chemical suppression. With a flow rate of 0.3mL per minute the anions F^-, Cl^-, NO_2^-, Br^-, NO_3^-, and SO_4^{2-} are eluted between 3.5 and 25 minutes. Each ion concentration is calculated from peak areas using a 25μL injection and compared to calibration graphs generated from a set of mixed standards with a range of concentrations

Trace elements

All trace elements were analysed by the CSIRO Analytical Services Unit (Waite Campus, SA).

Total P, S and trace elements were determined following US EPA (2007) microwave-assisted acid digestion of sediments, sludges, soils and oils. The finely ground sample was digested in a microwave oven using a mixture of nitric acid and hydrochloric acid. The solution was then analysed by inductively coupled plasma optical emission spectrometry (ICP-OES) for the following elements in water and sediment extracts: Al, As, B, Br, Cd, Cl, Co, Cr, Cu, F, Fe, Mn, Mo, Ni, P, Pb, Sb, Se, Si, Sr, V and Zn.

Chlorophyll *a*

Chlorophyll *a* was analysed in CSIRO Land and Water laboratories (Waite Campus) following methodology developed in-house.

Filter papers were cut into small pieces, placed into glass scintillation vials and had 5 mL cold 80% acetone solution added and were kept in the dark at 4°C for 48 h. A 200 μL sub-sample was placed in a 96 well plate and measured spectrophotometrically at 470, 646, 663 and 750 nm. The final calculation for chlorophyll A was:

Chlorophyll *a* = $12.25x(\Delta A_{663}-\Delta A_{470})-2.55x(\Delta A_{646}-\Delta A_{470})$

where ΔA_x is the blank corrected response at x nm.

Hormones

Hormones were analysed in CSIRO Land and Water laboratories (Waite Campus) following methodology developed in-house. Water samples were filtered through 0.3 μm glass fibre filters and 50 μL of 1 mg/L stable isotope solution (containing stable isotopes of estradiol, 17α-ethinylestradiol, estrone, testosterone and androstenedione) was added to each 500 mL sample. Sample were then passed through pre-conditioned Waters HLB solid phase extraction (SPE) cartridges and the cartridges were dried and stored at -18°C until analysis. On the day of analysis, SPE cartridges were eluted using 2x3 mL methanol and 2x3 mL dichloromethane into glass culture tubes. Solvents were dried and samples reconstituted in 1 mL dichloromethane and passed through Florisil cartridges for further clean-up. Collected samples were then evaporated and reconstituted in 400 μL pyridine and

100 μL N,O-bis(trimethylsilyl)trifluoroacetamide reagent (BSTFA) and derivatised for 1 hour at 60^{o}C. After cooling samples were transferred to GC-MS/MS for analysis.

Sediment samples for hormone analysis were freeze-dried and 1 g sub-samples were extracted ultrasonically with 2x5 mL methanol and 5 mL acetone. Solvent extracts were then combined and dried. Solvent extracts were then reconstituted in dichloromethane and treated as per water samples.

Samples were then analysed using an Agilent 7890A GC-MS/MS system.

fDOC

DOC fluorescence was analysed at University of NSW Department of Civil and Environmental Engineering (Sydney, NSW) following the methods outlined in Hambly et al (2010). Water samples were sent overnight on ice upon return from the field.

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Appendix 4. Summary of historical data

Table A 2. Summary of historical data collated for LEB

River/catchment	Location	Sample year	Number of samples	Parameter	Value	ANZECC value[a]	Source
Alice River/ Cooper	Barcaldine	1972-2009	1-17	Total N	1.05±0.35 mg/L		1
				TKN	0.6 mg/L		
				NO_3-N	1.62±0.89 mg/L		
				DO	5.49±2.19 mg/L		
				Total P	0.074±0.032 mg/L		
Barcoo River/ Cooper	Blackhall	1976-2010	2-41	Total N	0.86±0.48 mg/L		2
				NO_3-N	1.09±0.76 mg/L		
				NH_4^+	0.044±0.029 mg/L		
				DO	7.05±1.27 mg/L		
				Total P	0.39±0.35 mg/L		
				PO_4^{3-}	0.055±0.009 mg/L		
Barcoo River/ Cooper	Bulloo Bulloo waterhole	1994-1995	5	Alkalinity	102 mg/L		1
				HCO_3^-	92±53.8 mg/L		
				CO_3^{2-}	18 mg/L		
				EC	220.25±89.9 uS/cm		
				pH	8.2		
				TDS	120±49.3 mg/L		
				Turbidity	279±225 NTU		
				TKN	1.03±0.31 mg/L		
				NO_x	0.15±0.13 mg/L		
				Total P	0.27±0.18 mg/L		
				SO_4^{2-}	12.1±2.09 mg/L		
				Na	22.5±9.96 mg/L		
				K	6.94±2.68 mg/L		
				Ca	16.1±6.29 mg/L		
				Mg	6.3±2.51 mg/L		
Barcoo River/ Cooper	Retreat	2001	3	DO	7.6±0.6 mg/L		2

Barcoo River/ Cooper	Wellford	1995	1	EC	138 μS/cm		3
				DO	4 mg/L		
				TKN	0.6 mg/L		
				Total P	0.22 mg/L		
Cooper Creek/ Cooper	Coongie Crossing	2012	1	Chlorophyll a	28.9 μg/L		1
				TKN	2.22 mg/L		
				NO_3^-	0.788 mg/L		
				Total P	0.527 mg/L		
Cooper Creek/ Cooper	Cullyamurra Waterhole	1972-2012	225	Chlorophyll a	11.8 μg/L	-	1
				Alkalinity	70.6±18.9 mg/L	-	
				Al	0.80±3.6 mg/L	0.055 mg/L	
				NH_4^+	0.24±0.32 mg/L	0.1 mg/L	
				HCO_3^-	83.5±24.4 mg/L	-	
				B	0.11±0.069 mg/L	0.68 mg/L	
				Br	0.84±0.73 mg/L	-	
				Ca	14.3±4.7 mg/L	-	
				Total C	31 mg/L	-	
				Organic C	5.68±1.28 mg/L	-	
				Cl	14.5 mg/L	-	
				Cr	0.02 mg/L	0.06 mg/L (Cr VI)	
				EC	198 uS/cm	100-5000 μS/cm	
				Cu	0.01±0.01 mg/L	0.0018 mg/L	
				DO	7.61±2.13 mg/L	90% (8.2 mg/L @ 20°C)	
				Fe	54.3±20.5 mg/L	-	
				Pb	9.75±9.03 mg/L	0.0056 mg/L	
				Mg	5.51±3.72 mg/L	-	
				Mn	0.06±0.03 mg/L	2.5 mg/L	
				Ni	0.039±0.032 mg/L	0.013 mg/L	
				NO_3^-	0.37±0.37 mg/L	0.1 mg/L	
				pH	7.67±0.48	6.5-9 (lower-upper)	
				Total P	0.525 mg/L	0.1 mg/L	
				K	5.66±1.01 mg/L	-	
				Si	13.9±5.3 mg/L	-	
				Na	19.6±4.78 mg/L	-	
				SO_4^{2-}	13±7.2 mg/L	-	
				TSS	66.8±43 mg/L	-	

				TKN	1.12±0.46 mg/L	-	
				TDS	109±62 mg/L	-	
				Turbidity	376±237 NTU	1-100 NTU	
				Zn	0.03±0.02 mg/L	0.008 mg/L	
Cooper Creek/ Cooper	Currareva	1995	1	EC	124 μS/cm	100-5000 μS/cm	3
				DO	2.4 mg/L	90% (8.2 mg/L @ 20°C)	
				TKN	2.1 mg/L	-	
				Total P	0.79 mg/L	0.1 mg/L	
Cooper Creek/ Cooper	Embarka waterhole	1994-2012	8	Chlorophyll A	2.79 μg/L	-	1
				Alkalinity	99.1 mg/L	-	
				HCO_3^-	144±27.8 mg/L	-	
				CO_3^{2-}	12 mg/L	-	
				EC	303±52.8 μS/cm	100-5000 μS/cm	
				pH	7.6	6.5-9 (lower-upper)	
				TDS	166±29 mg/L	-	
				Turbidity	151±96.4 NTU	1-100 NTU	
				TKN	1.265±0.44 mg/L	-	
				NO_x	0.15±0.19 mg/L	0.1 mg/L	
				Total P	0.164±0.1 mg/L	0.1 mg/L	
				SO_4^{2-}	15.8±1.94 mg/L	-	
				Na	28.4±6.43 mg/L	-	
				K	8.89±1.18 mg/L	-	
				Ca	24.5±4.52 mg/L	-	
				Mg	8.13±1.58 mg/L	-	
				Cl	15±4.24 mg/L	-	
Cooper Creek/ Cooper	Glen Murken waterhole	2001	1	Alkalinity	1.52 mEq/L	-	4
				pH	7.5	6.5-9 (lower-upper)	
				Turbidity	266 NTU	1-100 NTU	
				Total N	1.2 mg/L	1 mg/L	
				NO_3	0.5 mg/L	0.1 mg/L	
				Total P	0.27 mg/L	0.1 mg/L	
Cooper Creek/ Cooper	Innamincka	1974-2012	20	Chlorophyll a	8.78 μg/L	-	1
				Alkalinity	89.2±0.67 mg/L	-	
				HCO_3^-	75±22.1 mg/L	-	
				CO_3^{2-}	20±18.3 mg/L	-	
				EC	183±107 μS/cm	100-5000 μS/cm	

				pH	8.7±0.2	6.5-9 (lower-upper)	
				TDS	113±47.3 mg/L	-	
				Turbidity	219±202 NTU	1-100 NTU	
				Total C	34 mg/L	-	
				Organic C	12 mg/L	-	
				TKN	1.144±0.83 mg/L	-	
				NO_3^-	0.289 mg/L	0.1 mg/L	
				NH_4^+	0.07	0.1 mg/L	
				Total P	0.066±0.047 mg/L	0.1 mg/L	
				SO_4^{2-}	10.8±2.74 mg/L	-	
				Na	23.2±15.3 mg/L	-	
				K	6.85±1.63 mg/L	-	
				Ca	14.3±3.68 mg/L	-	
				Mg	5.41±1.69 mg/L	-	
				B	0.1 mg/L	0.68 mg/L	
				Cl	15.2±7.41 mg/L	-	
				Fe	5.4 mg/L	-	
				Si	9 mg/L	-	
Cooper Creek/ Cooper	Kings waterhole	2012	1	Chlorophyll a	6.87 μg/L	-	1
				TKN	1.47 mg/L	-	
				NO_3^-	0.249 mg/L	0.1 mg/L	
				Total P	0.444 mg/L	0.1 mg/L	
Cooper Creek/ Cooper	Kopperamanna ferry	1974-1977	24	Alkalinity	123±50.2 mg/L	-	1
				HCO_3^-	150±61.2 mg/L	-	
				EC	1209±1762 uS/cm	100-5000 μS/cm	
				pH	7.45±0.31	6.5-9 (lower-upper)	
				TDS	701±1054 mg/L	-	
				Turbidity	47.4±11.97 NTU	1-100 NTU	
				TKN	2.854±0.61 mg/L	-	
				Total P	0.136±0.14 mg/L	0.1 mg/L	
				SO_4^{2-}	62.4±85.2 mg/L	-	
				Na	218±374 mg/L	-	
				K	9.79±1.05 mg/L	-	
				Ca	24.3±11.8 mg/L	-	
				Mg	11.3±14.3 mg/L	-	
				B	0.426±0.41 mg/L	0.68 mg/L	

				Cl	288±531 mg/L	-	
				Fe	0.50±0.48 mg/L	-	
				Si	11.3±4.6 mg/L	-	
Cooper Creek/ Cooper	Kudramitchie waterhole	2012	1	Chlorophyll a	51.8 μg/L	-	1
				TKN	2.78 mg/L	-	
				NO_3^-	0.398 mg/L	0.1 mg/L	
				Total P	2.48 mg/L	0.1 mg/L	
Cooper Creek/ Cooper	Minkie Waterhole	2012	1	Chlorophyll a	10.8 μg/L	-	1
				TKN	2.78 mg/L	-	
				NO_3^-	0.142 mg/L	0.1 mg/L	
				Total P	0.599 mg/L	0.1 mg/L	
Cooper Creek/ Cooper	Monkira	1995	1	EC	144 μS/cm	100-5000 μS/cm	3
				DO	2.8 mg/L	90% (8.2 mg/L @ 20°C)	
				TKN	1.1 mg/L	-	
				Total P	0.96 mg/L	0.1 mg/L	
Cooper Creek/ Cooper	Nappa Merrie	1977-2012	1-25	Total N	1.35±0.54 mg/L	1 mg/L	2
				TKN	1.22	-	
				NO_3-N	2.28±2.23 mg/L	0.1 mg/L	
				NH_4^+	0.009±0.007 mg/L	0.1 mg/L	
				DO	7.38±3.12 mg/L	90% (8.2 mg/L @ 20°C)	
				Total P	0.38±0.15 mg/L	0.1 mg/L	
				PO_4^{3-}	0.069±0.03mg/L	0.04 mg/L	
Cooper Creek/ Cooper	Scrubby Camp waterhole	2012	1	Chlorophyll A	8.84 μg/L	-	1
				TKN	1.78mg/L	-	
				NO_3^-	0.803 mg/L	0.1 mg/L	
				Total P	0.526mg/L	0.1 mg/L	
Cooper Creek/ Cooper	Tirrawarra waterhole	1994-1995	6	Alkalinity	86.8 mg/L	-	1
				HCO_3^-	102±29 mg/L	-	
				CO_3^{2-}	3.3 mg/L	-	
				EC	228±67. uS/cm	100-5000 μS/cm	
				pH	7.8	6.5-9 (lower-upper)	
				TDS	125±36.8 mg/L	-	
				Turbidity	324±111 NTU	1-100 NTU	
				TKN	1.04±0.33 mg/L	-	
				NO_x	0.385±0.14 mg/L	0.1 mg/L	
				Total P	0.099±0.04 mg/L	0.1 mg/L	

				SO_4^{2-}	14.7±3.92 mg/L	-	
				Na	21.1±5.52 mg/L	-	
				K	7.26±1.6 mg/L	-	
				Ca	18.9±4.51 mg/L	-	
				Mg	6.66±1.1 mg/L	-	
				Cl	13.7±5.43 mg/L	-	
Cooper Creek/ Cooper	Windorah	2006	1	HCO_3^-	66.6 mg/L	-	5
				CO_3^{2-}	0.08 mg/L	-	
				pH	7.39	6.5-9 (lower-upper)	
				TDS	116 mg/L	-	
				SO_4^{2-}	11 mg/L	-	
				Na	8.6	-	
				K	3.3 mg/L	-	
				Ca	10.6 mg/L	-	
				Mg	2.5 mg/L	-	
				Cl	3.5 mg/L	-	
Cooper Creek/ Cooper	Various	2001-2004	39	Hardness	76.8±5.8 mg/L	-	4
				EC	346±39 µS/cm	100-5000 µS/cm	
				pH	7.6±0.04	6.5-9 (lower-upper)	
				TDS	206±23.2 mg/L	-	
				TSS	364±82.9 mg/L	-	
				Turbidity	725±152 NTU	1-100 NTU	
				Total N	2.9±0.49 mg/L	0.1 mg/L	
				Total P	0.7±0.09 mg/L	0.1 mg/L	
Cornish Creek/ Cooper	Bowen Downs	1976-2007	2-11	Total N	0.56±0.08 mg/L	1 mg/L	2
				NO_3-N	1.49±0.96 mg/L	0.1 mg/L	
				NH_4^+	0.021±0.004 mg/L	0.1 mg/L	
				DO	7.9±2.2 mg/L	90% (8.2 mg/L @ 20°C)	
				Total P	0.084±0.004 mg/L	0.1 mg/L	
				PO_4^{3-}	0.006±0.001 mg/L	0.04 mg/L	
Darr River/ Cooper	Darr	1974-2000	3-17	NO_3-N	1.52±0.69 mg/L	0.1 mg/L	2
				DO	7.36±1.91 mg/L	90% (8.2 mg/L @ 20°C)	
				K	3.56±0.76 mg/L	-	
Thomas River/ Cooper	Stonehenge	1978-2004	2-16	Total N	0.83±0.17 mg/L	1 mg/L	2
				NO_3-N	1.06±0.81 mg/L	0.1 mg/L	
				DO	6.54±1.63 mg/L	90% (8.2 mg/L @ 20°C)	

				Total P	0.37±0.16 mg/L	0.1 mg/L	
Thomson River/ Cooper	Jundah	2006	1	HCO_3^-	66.6 mg/L	-	5
				CO_3^{2-}	0.08 mg/L	-	
				pH	7.42	6.5-9 (lower-upper)	
				TDS	138 mg/L	-	
				SO_4^{2-} mg/L	19	-	
				Na mg/L	15.3	-	
				K mg/L	3.4	-	
				Ca mg/L	12.3	-	
				Mg mg/L	3.1	-	
				Cl mg/L	8.1	-	
Thomson River/ Cooper	Lochern	1995	1	EC	140 µS/cm	100-5000 µS/cm	3
				DO	5.8 mg/L	90% (8.2 mg/L @ 20°C)	
				TKN	0.9 mg/L	-	
				Total P	0.36 mg/L	0.1 mg/L	
Thomson River/ Cooper	Longreach	1995-2010	3-48	Total N	0.637±0.22 mg/L	1 mg/L	2
				TKN	0.91±0.52 mg/L	-	
				NO_3-N	1.43±0.98 mg/L	0.1 mg/L	
				NH_4^+	0.046±0.04 mg/L	0.1 mg/L	
				DO	6.52±1.76 mg/L	90% (8.2 mg/L @ 20°C)	
				Total P	0.29±0.16 mg/L	0.1 mg/L	
				PO_4^{3-}	0.064±0.023 mg/L	0.04 mg/L	
Warrego River/ Cooper	Various	2001-2004	31	Hardness	42.9±2.8 mg/L	-	4
				EC	252±44.3 µS/cm	100-5000 µS/cm	
				pH	7.42±0.07	6.5-9 (lower-upper)	
				TDS	151±26.2 mg/L	-	
				TSS	181±26.4 mg/L	-	
				Turbidity	755±87 NTU	1-100 NTU	
				Total N	1.5±0.18 mg/L	1 mg/L	
				Total P	0.7±0.16 mg/L	0.1 mg/L	
Diamantina River/ Diamantina	Birdsville	1971-2012	39	Chlorophyll a	9.92 µg/L	-	1
				Alkalinity mg/L	44.9±12.6 mg/L	-	
				HCO_3^-	54.7±15.4 mg/L	-	
				DO	7.24±0.5 mg/L	90% (8.2 mg/L @ 20°C)	
				EC	134±44.8 uS/cm	100-5000 µS/cm	
				pH	7.6±0.299	6.5-9 (lower-upper)	

				TDS	58.5±12.5 mg/L	-	
				Turbidity	557±316 NTU	1-100 NTU	
				Total C	20±2.82 mg/L	-	
				Organic C	6±5.29 mg/L	-	
				TKN	1.35±0.965 mg/L	-	
				NO_x	0.088±0.041 mg/	0.1 mg/L	
				NH_4^+	0.284±0.294	0.1 mg/L	
				Total P	0.194±0.029 mg/L	0.1 mg/L	
				SO_4^{2-}	9.12±4.39 mg/L	-	
				Na	15.6±7.01 mg/L	-	
				K	5.31±3.2 mg/L	-	
				Ca	7.12±3.44 mg/L	-	
				Mg	3.25±1.39 mg/L	-	
				B	0.07±0.07 mg/L	0.68 mg/L	
				Cl	6±6 mg/L	-	
				Fe	26.8±28.29 mg/L	-	
				Si	22.2±14 mg/L	-	
Diamantina River/ Diamantina	Clifton Hills	2012	1	Chlorophyll a	15.6 μg/L	-	1
				TKN	2.41 mg/L	-	
				NO_3^-	1.28 mg/L	0.1 mg/L	
				Total P	1.02 mg/L	0.1 mg/L	
Derwent Creek/ Diamantina	Cowarie Homestead	2012	1	Chlorophyll a	31.1 μg/L	-	1
				TKN	5.18 mg/L	-	
				NO_3^-	0.01 mg/L	0.1 mg/L	
				Total P	0.499 mg/L	0.1 mg/L	
Diamantina River/ Diamantina	Davenport Downs	1995	1	EC	121 μS/cm	100-5000 μS/cm	3
				DO	3.8 mg/L	90% (8.2 mg/L @ 20°C)	
				TKN	0.7 mg/L	-	
				Total P	0.69 mg/L	0.1 mg/L	
Diamantina River/ Diamantina	Diamantina Lakes	1973-2004	11	Total N	1.05±0.64 mg/L	0.1 mg/L	2,3
				TKN	1.35 mg/L	-	
				NO_3-N	2.87±1.65 mg/L	0.1 mg/L	
				Total P	0.48±0.17 mg/L	0.1 mg/L	
				DO	8.62±0.67 mg/L	90% (8.2 mg/L @ 20°C)	
				K	3.16±0.8 mg/L	-	
				EC	90 μS/cm	100-5000 μS/cm	

				TKN	1.3 mg/L	-	
				Total P	1.8 mg/L	0.1 mg/L	
Diamantina River/ Diamantina	Old Cork	1995	1	EC	103 µS/cm	100-5000 µS/cm	3
				DO	2.6 mg/L	90% (8.2 mg/L @ 20^{o}C)	
				TKN	0.6 mg/L	-	
				Total P	0.49 mg/L	0.1 mg/L	
Diamantina River/ Diamantina	Pandie Pandie	2012	1	Chlorophyll a	3.53 µg/L	-	1
				TKN	1.71 mg/L	-	
				NO_3^-	1.08 mg/L	0.1 mg/L	
				Total P	0.686 mg/L	0.1 mg/L	
Warburton River/ Diamantina-Georgina	Cowarie Crossing	2012	1	Chlorophyll a	24.3 µg/L	-	1
				TKN	0.74 mg/L	-	
				NO_3^-	0.005 mg/L	0.1 mg/L	
				Total P	0.068 mg/L	0.1 mg/L	
Warburton River/ Diamantina-Georgina	Yelpawaralinna	2003-2012	17	Chlorophyll a	7.75 µg/L	-	1
				Alkalinity	170±204 mg/L	-	
				HCO_3^-	208±250 mg/L	-	
				DO	8.84±1.31 mg/L	90% (8.2 mg/L @ 20^{o}C)	
				EC	1560 uS/cm	100-5000 µS/cm	
				pH	8.39±0.47	6.5-9 (lower-upper)	
				TDS	230±180 mg/L	-	
				Turbidity	1075±1020 NTU	1-100 NTU	
				Organic C	30.2±21.7 mg/L	-	
				TKN	2.73±3.51 mg/L	-	
				NO_x	1.03±0.98 mg/L	0.1 mg/L	
				Total P	0.69±0.45 mg/L	0.1 mg/L	
				SO_4^{2-}	30.8±12.5 mg/L	-	
				Na	43.2±16.2 mg/L	-	
				K	6.42±2.14 mg/L	-	
				Ca	15.2±4.56 mg/L	-	
				Mg	5.88±1.35 mg/L	-	
				Al	2.72±4.1 mg/L	0.055 mg/L	
				Cl	19.6±3.85 mg/L	-	
				Cu	0.022±0.008 mg/L	0.0018 mg/L	
				Fe	35.9±22 mg/L	-	
				Pb	0.009±0.004 mg/L	0.0034 mg/L	

				Si	24.2±8.74 mg/L	-	
				Zn	0.005±0.001 mg/L	0.008 mg/L	
Georgina Diamantina Cooper Bulloo	Various (30 sites)	1997-1999	72	DO EC pH Turbidity Total N Total P	3.3-14 mg/L 52-620 µS/cm 6.7-9 4-1000 NTU 0.3-3 mg/L 0.03-0.85 mg/L	90% (8.2 mg/L @ 20°C) 100-5000 µS/cm 6.5-9 (lower-upper) 1-100 NTU 1 mg/L 0.1 mg/L	7
Margaret River/ Western LEB	Oodnadatta Track	2003-2007	15	Alkalinity HCO_3^- DO EC pH TDS Turbidity Organic C TKN NO_x Total P SO_4^{2-} Na K Ca Mg Al Cl Cu Fe Pb Si Zn	73.8±35.6 mg/L 90.2±43.3 mg/L 8.57±2.34 mg/L 8040 uS/cm 8.3±0.349 43128±48535 mg/L 20.2±26.2 NTU 5.4 mg/L 0.98±0.62 mg/L 0.022±0.032 mg/L 0.021±0.024 mg/L 4608±3594 mg/L 16003±13535 mg/L 104±89.2 mg/L 1272±1175 mg/L 1529±1798 mg/L 0.0283 mg/L 28702±25176 mg/L 0.0198±0.0187 mg/L 0.628±0.101 mg/L 0.0017 mg/L 5.12±2.75 mg/L 0.0712±0.011 mg/L	- - 90% (8.2 mg/L @ 20°C) 100-5000 µS/cm 6.5-9 (lower-upper) - 1-100 NTU - - 0.1 mg/L 0.1 mg/L - - - - - 0.055 mg/L - 0.0014 mg/L - 0.0034 mg/L - 0.008 mg/L	1
Neales River/ western LEB	Algebuckina Waterhole	2003-2007	27	Alkalinity HCO_3^- CO_3^{2-} DO EC	82±19.7 mg/L 99±23.5 mg/L 3.5±2.12 mg/L 11±2.18 mg/L 525 uS/cm	- - - 90% (8.2 mg/L @ 20°C) 100-5000 µS/cm	1

				pH	8.6±0.64	6.5-9 (lower-upper)	
				TDS	3935±2201 mg/L	-	
				Turbidity	49.4±132.2 NTU	1-100 NTU	
				Organic C	10.7±4.2 mg/L	-	
				TKN	1.38±0.79 mg/L	-	
				NO_x	0.096±0.21 mg/L	0.1 mg/L	
				Total P	0.022±0.032 mg/L	0.1 mg/L	
				SO_4^{2-}	984±433 mg/L	-	
				Na	1863±898 mg/L	-	
				K	32.8±14.3 mg/L	-	
				Ca	116±38 mg/L	-	
				Mg	69.7±31.3 mg/L	-	
				Al	0.26 mg/L	0.055 mg/L	
				Cl	2607±1159 mg/L	-	
				Cu	0.003±0.002 mg/L	0.0014 mg/L	
				Fe	0.65±0.38 mg/L	-	
				Pb	0.0006 mg/L	0.0034 mg/L	
				Si	6.33±3.77 mg/L	-	
				Zn	0.027 mg/L	0.008 mg/L	
Yardaparinna Creek/ western LEB	Macumba	2003-2007	23	Alkalinity	120±68.5 mg/L	-	1
				HCO_3^-	147±83.5 mg/L	-	
				DO	8.85±3.15 mg/L	90% (8.2 mg/L @ 20°C)	
				EC	192 uS/cm	100-5000 µS/cm	
				pH	7.72±0.84	6.5-9 (lower-upper)	
				TDS	199±156 mg/L	-	
				Turbidity	105±113 NTU	1-100 NTU	
				Organic C	12.9±10 mg/L	-	
				TKN	1.96±1.25 mg/L	-	
				NO_x	0.101±0.15 mg/L	0.1 mg/L	
				Total P	0.026±0.03 mg/L	0.1 mg/L	
				SO_4^{2-}	62.87±62.2 mg/L	-	
				Na	79.2±61.9 mg/L	-	
				K	13.8±9.74 mg/L	-	
				Ca	26.3±24.9 mg/L	-	
				Mg	7.11±6.67 mg/L	-	
				Al	0.19±0.2 mg/L	0.055 mg/L	

	Cl	66.1±52.5 mg/L	-
	Cu	0.004±0.002 mg/L	0.0014 mg/L
	Fe	4.6±6.22 mg/L	-
	Pb	0.003±0.004 mg/L	0.0034 mg/L
	Si	8.83±4.17 mg/L	-
	Zn	0.005±0.001 mg/L	0.008 mg/L

[a]Period of sample collection; [b]ANZECC guideline trigger value for south central Australia with low rainfall (nutrients and water quality) or representing 95% species protection value (trace elements)

Source: 1) SA EPA

2) Queensland DNRM

3) Long PE, Humphery VE (1995) Fisheries study Lake Eyre catchment: Thomson and Diamantina drainages December 1995. Department of Primary Industries Queensland.

4) Fellows CS, Bunn SE, Sheldon F, Beard NJ (2009) Benthic metabolism in two turbid dryland rivers. Freshwater Biology 54: 236-253

5) Cendon DI, Larsen JR, Jones BG, Nanson GC, Rickleman D, Hankin SI, Pueyo JJ, Maroulis J (2010) Freshwater recharge into a shallow saline groundwater system, Cooper Creek floodplain, Queensland, Australia. Journal of Hydrology 392: 150-163

6) Sheldon F, Fellows CS (2010) Water quality in two Australian dryland rivers: spatial and temporal variability and the role of flow. Marine and Freshwater Research 61: 864-874

7) Choy SC, Thomson CB, Marshall JC (2002) Ecological condition of central Australian arid-zone rivers. Water Science and Technology 45: 225-232

Appendix 5. Summary of water quality data for collected samples

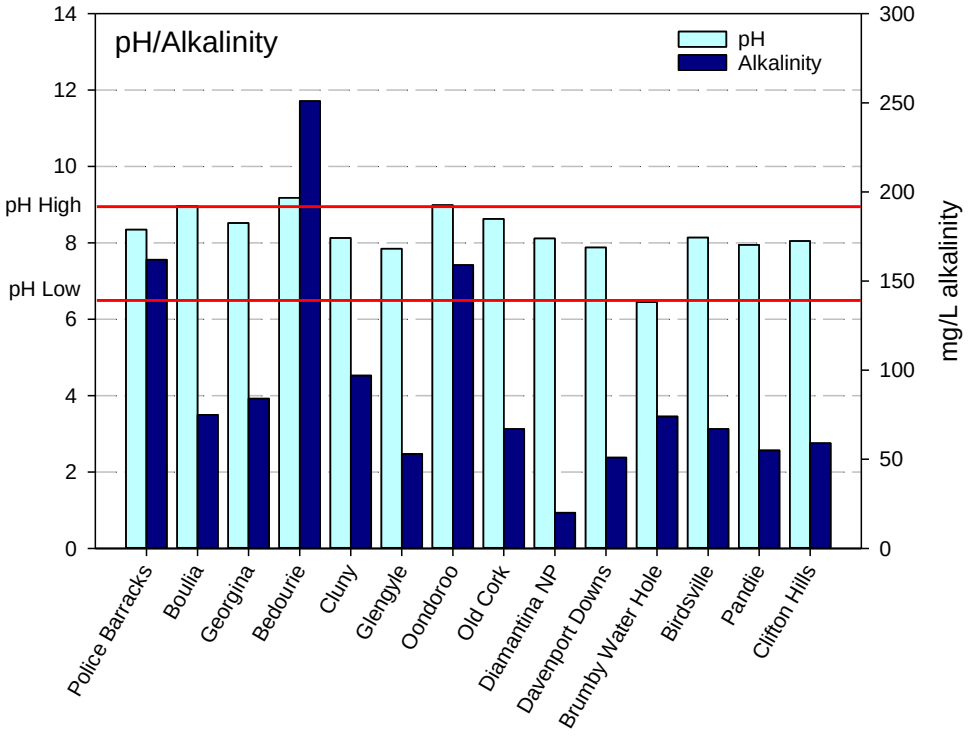

Figure A 1. Summary of pH and alkalinity in water samples. The lower and upper ANZECC/ARMCANZ default water quality guideline values are highlighted in red (south central Australia, low rainfall).

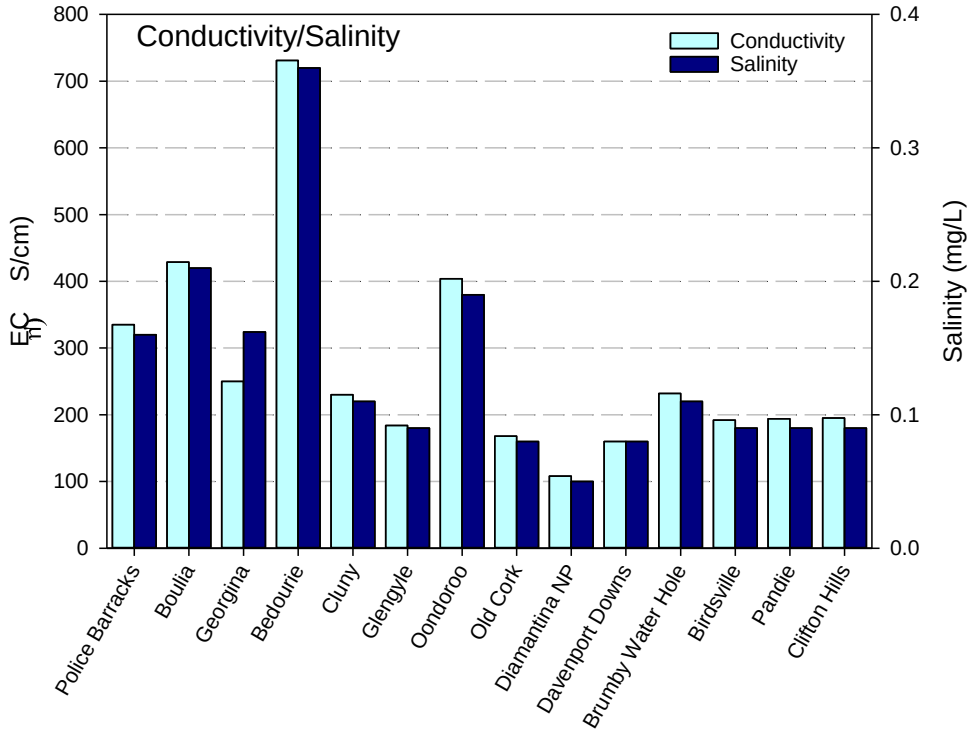

Figure A 2. Summary of EC and salinity in water samples. Maximum ANZECC/ARMCANZ default trigger value for EC is 5000 µS/cm.

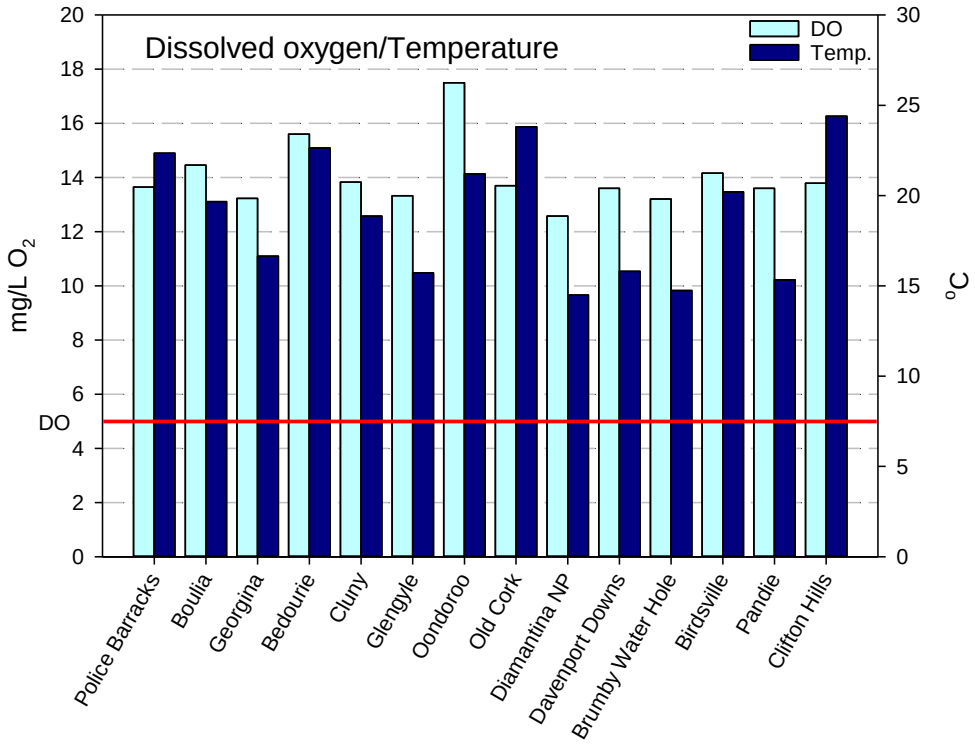

Figure A 3. Summary of DO and temperature in water samples. The lower ANZECC/ARMCANZ default water quality guideline value for DO is highlighted in red (south central Australia, low rainfall).

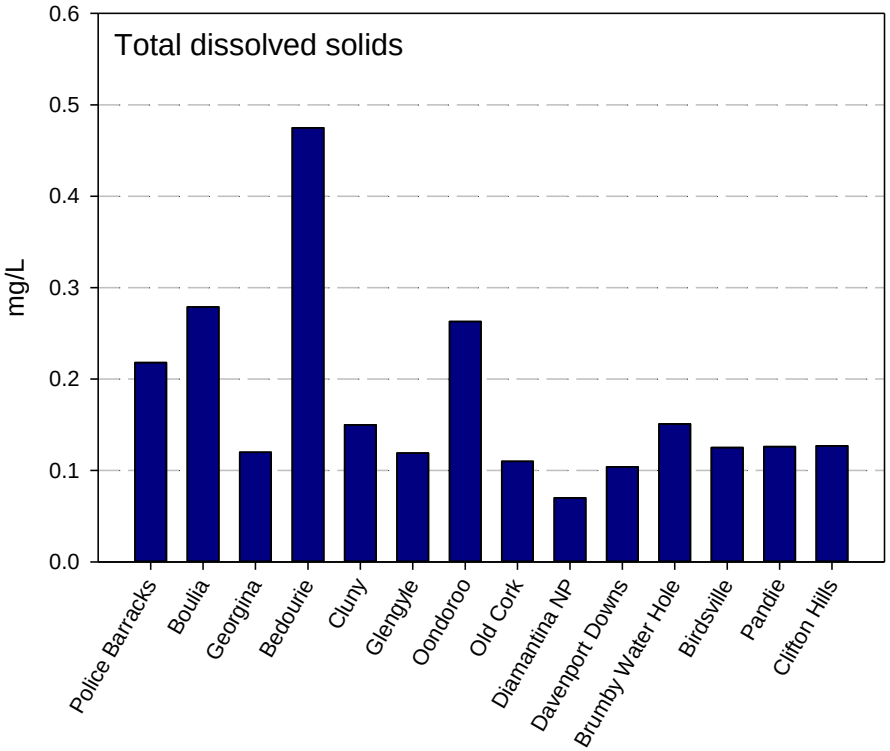

Figure A 4. Summary of TDS in water samples

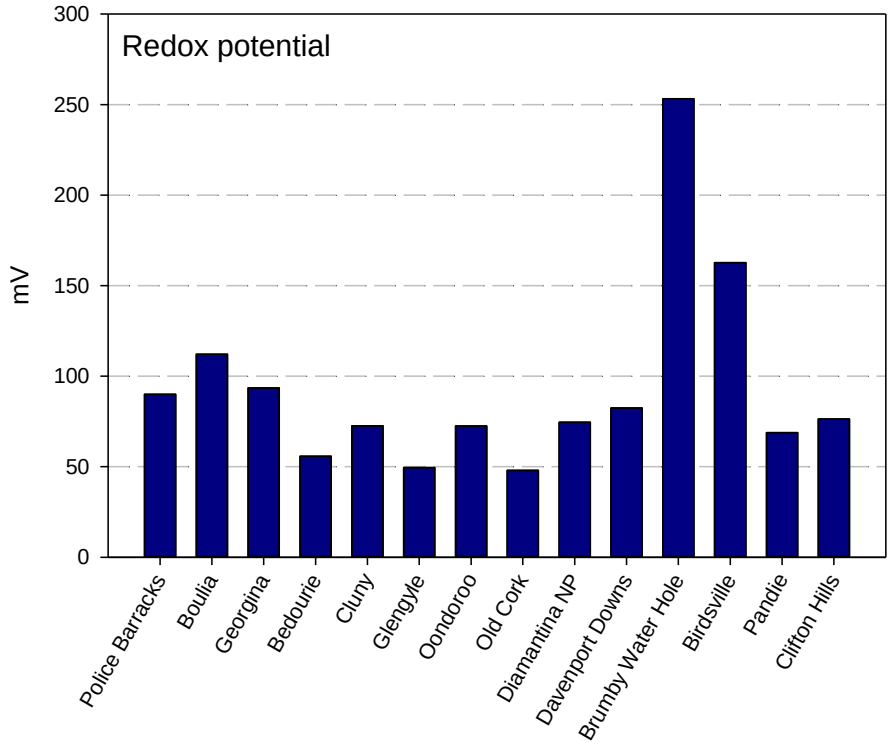

Figure A 5. Summary of redox potential in water samples

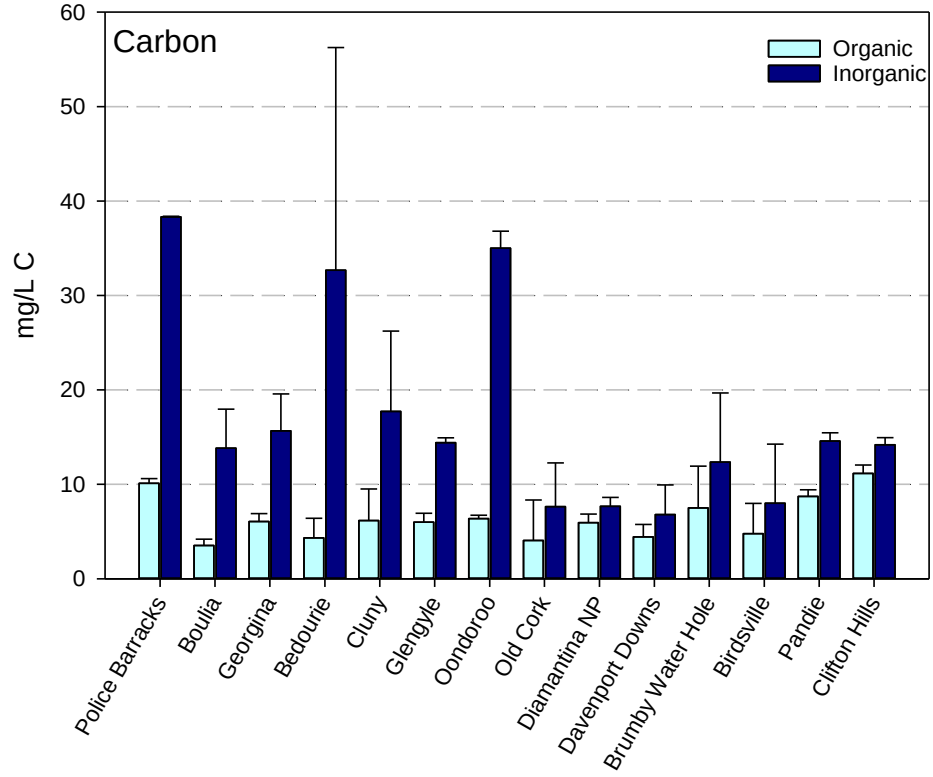

Figure A 6. Summary of carbon (organic and inorganic) in water samples

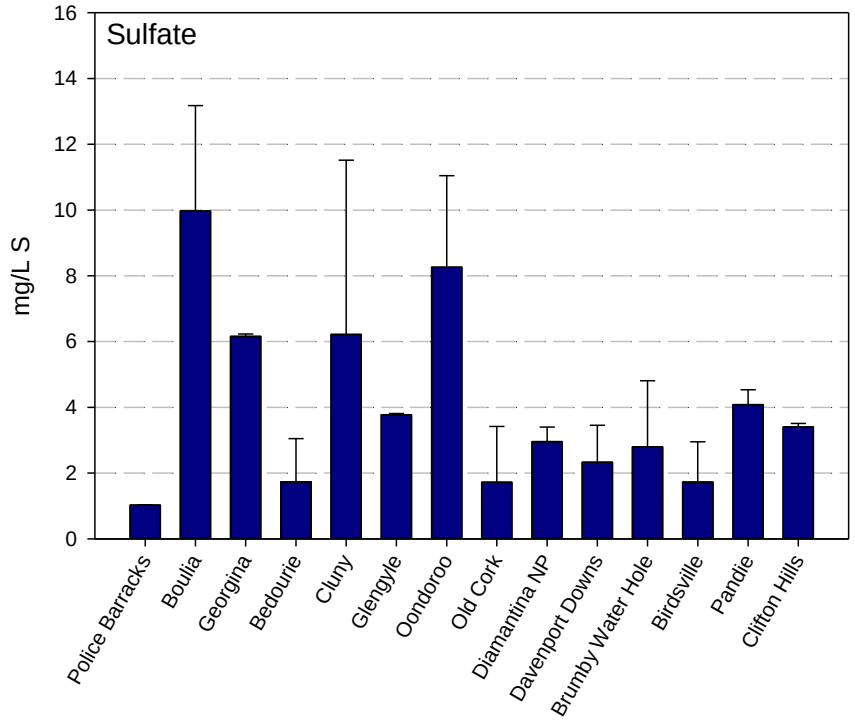

Figure A 7. Summary of sulfate (SO_4^{2-}) in water samples

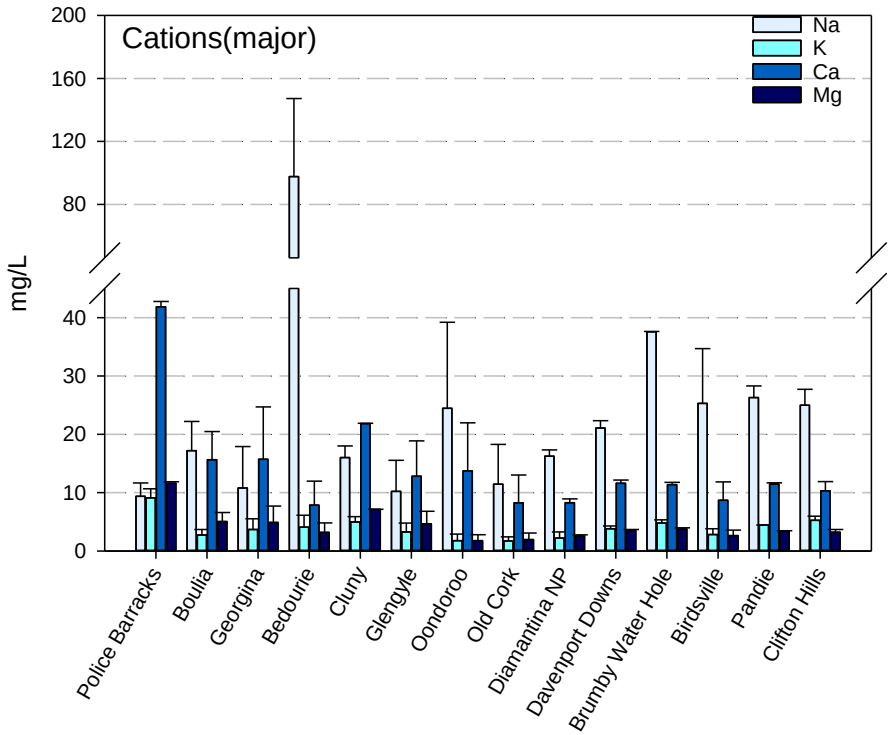

Figure A 8. Summary of major cations in water samples

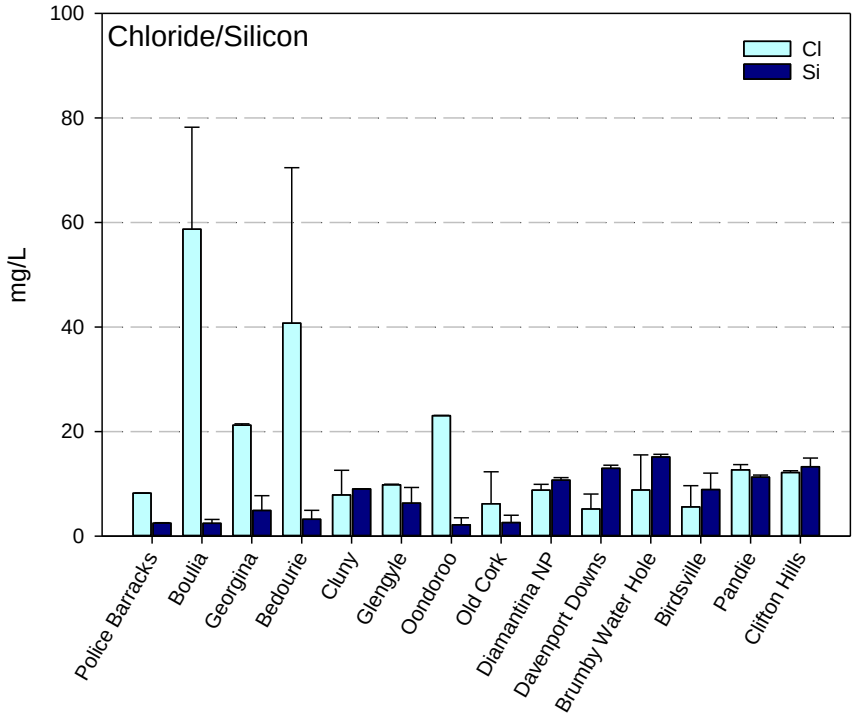

Figure A 9. Summary of chloride and silicon in water samples

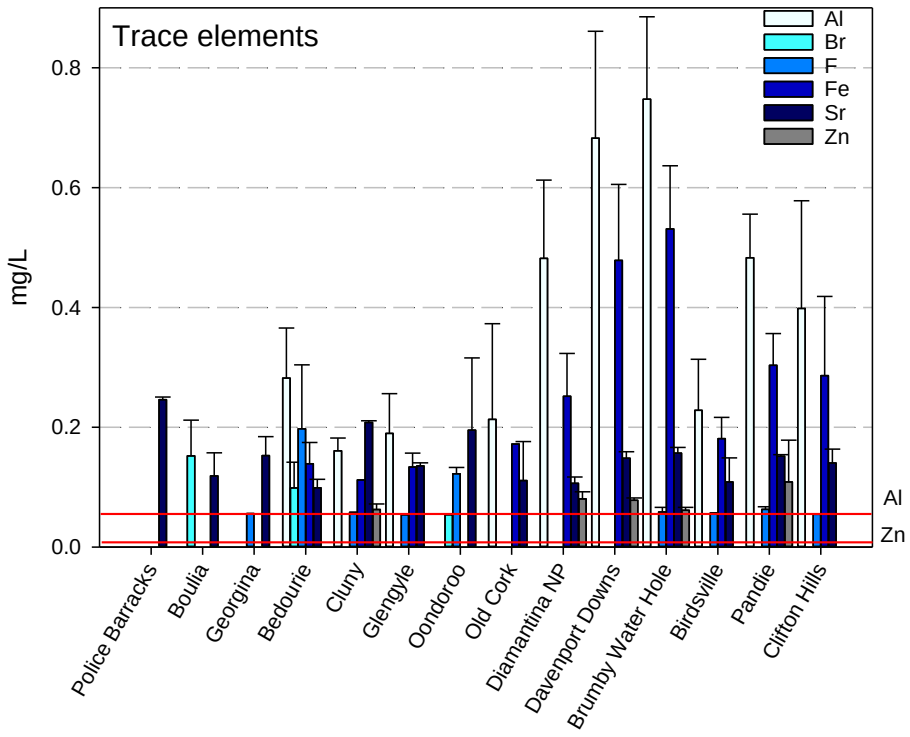

Figure A 10. Summary of trace elements in water samples. The ANZECC/ARMCANZ water quality guideline values for Al and Zn are highlighted in red (90% species protection level).

Appendix 5. Summary of sediment quality data for collected samples

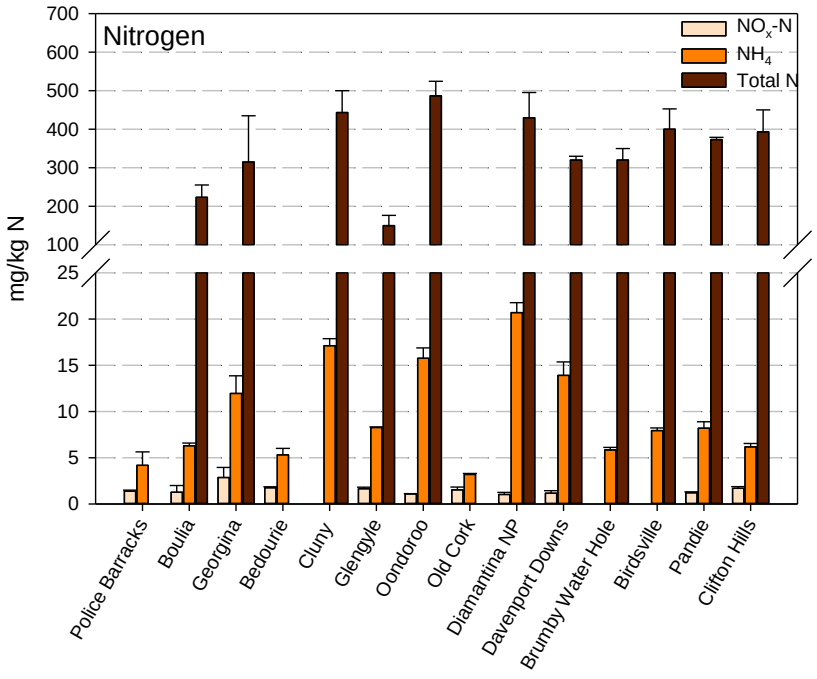

Figure A 11. Summary of nitrogen concentrations in sediment samples, including total nitrogen (N), ammonium (NH_4^+) and the sum of oxides of nitrogen (NO_x)

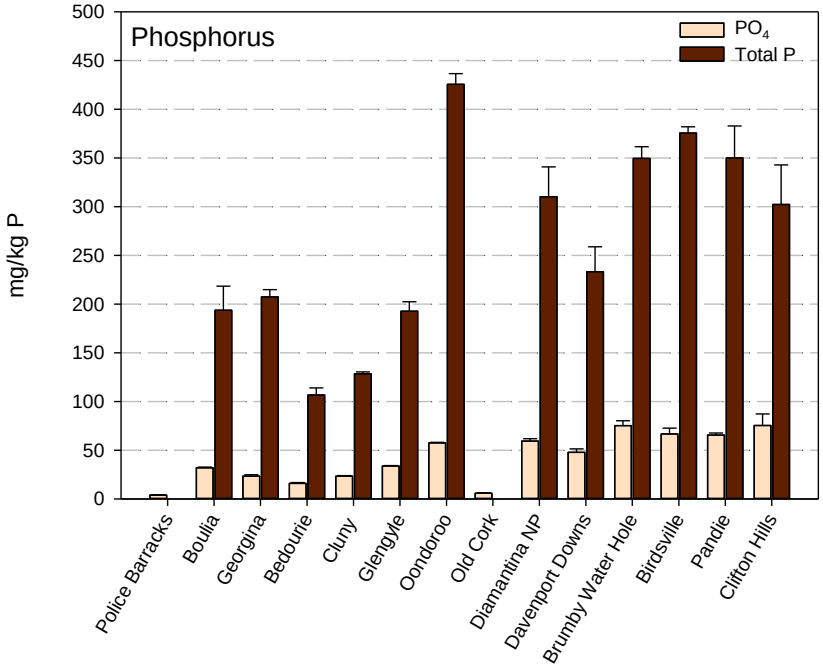

Figure A 12. Summary of phosphorus concentrations in sediment samples, including total phosphorus (P) and phosphate (PO_4).

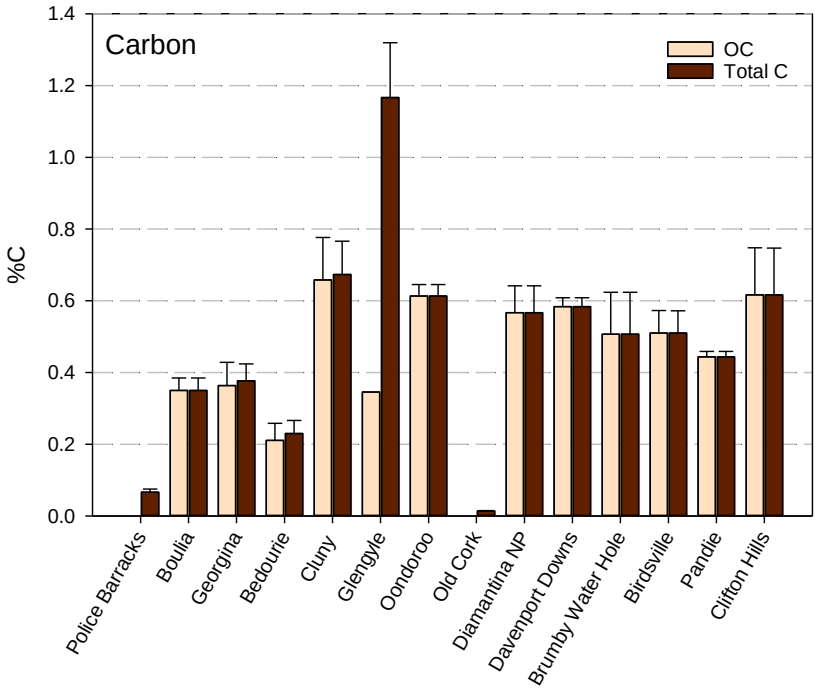

Figure A 13. Summary of carbon concentrations in sediment samples, including total carbon (C) and organic carbon (OC)

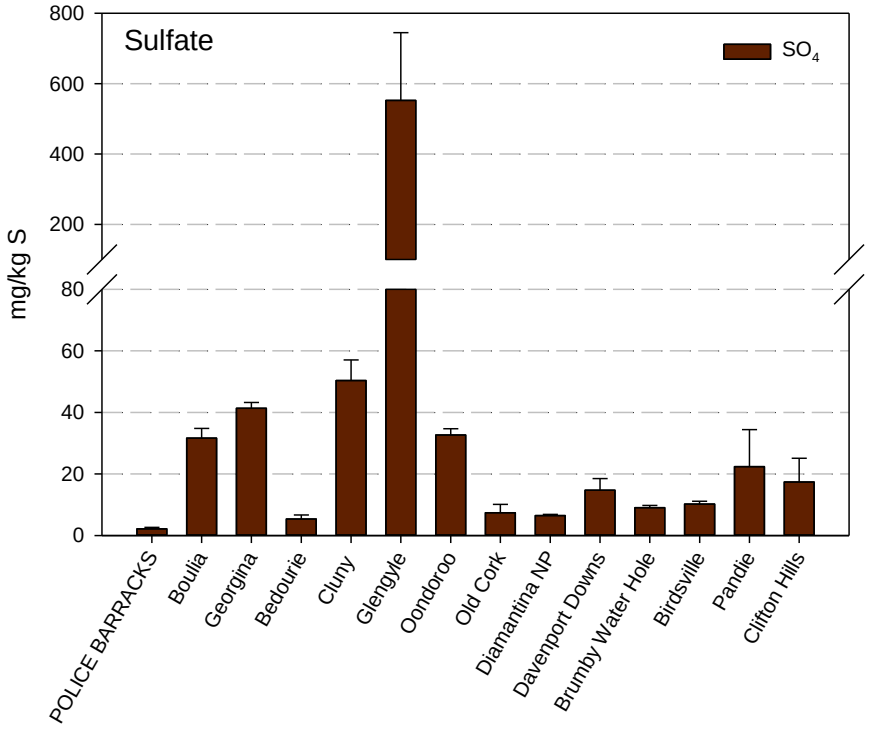

Figure A 14. Summary of sulfate concentrations in sediment samples

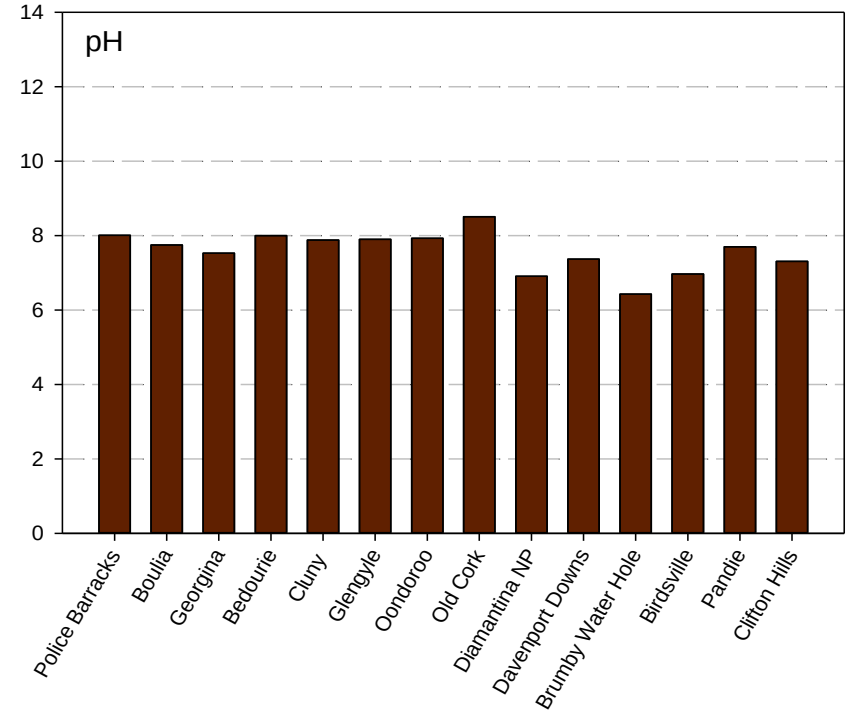

Figure A 15. Summary of pH in sediment samples

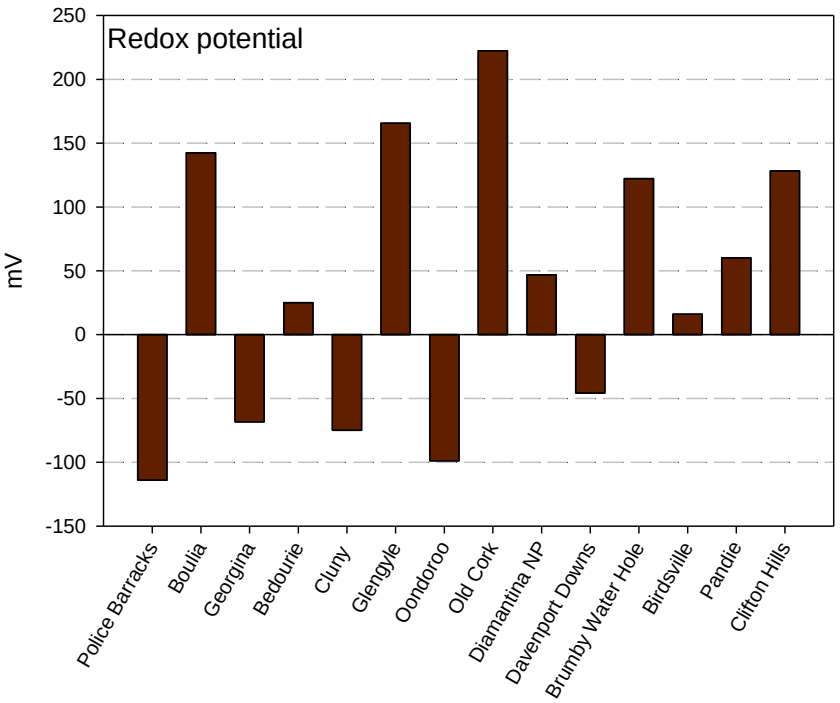

Figure A 16. Summary of redox potential of sediment samples

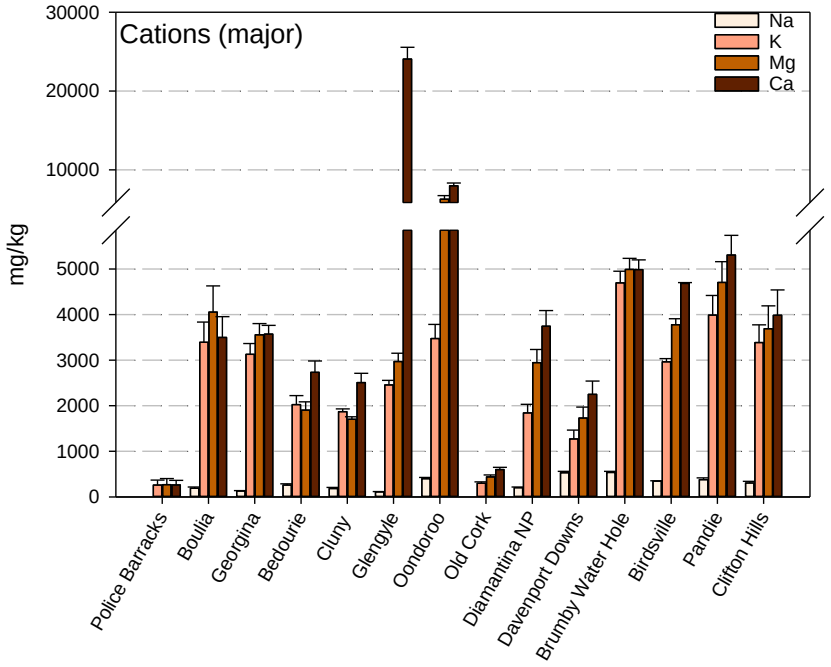

Figure A 17. Summary of major cations of sediment samples

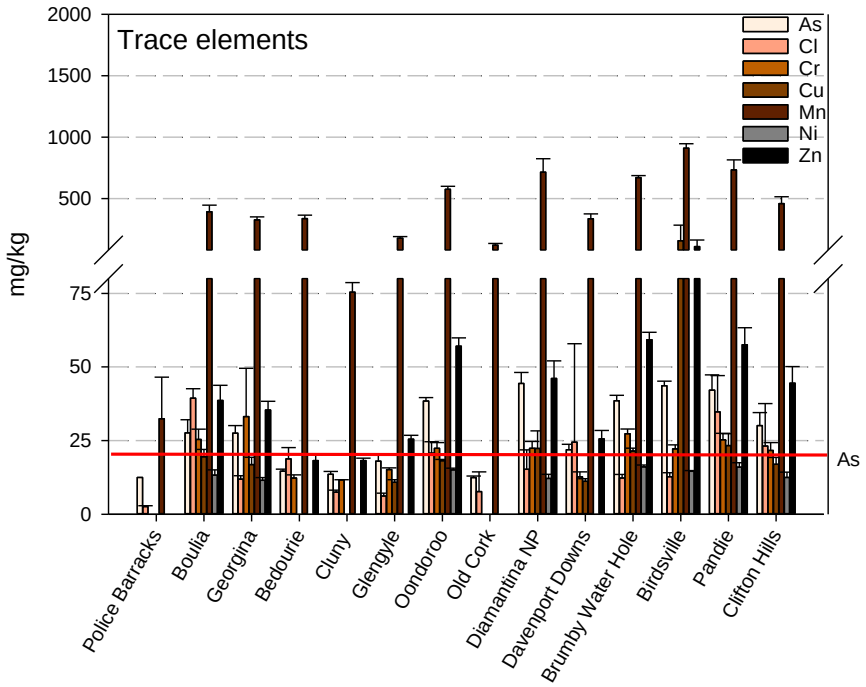

Figure A 18. Summary of trace elements in sediment samples. The ANZECC/ARMCANZ water quality guideline value for As are highlighted in red (90% species protection level).

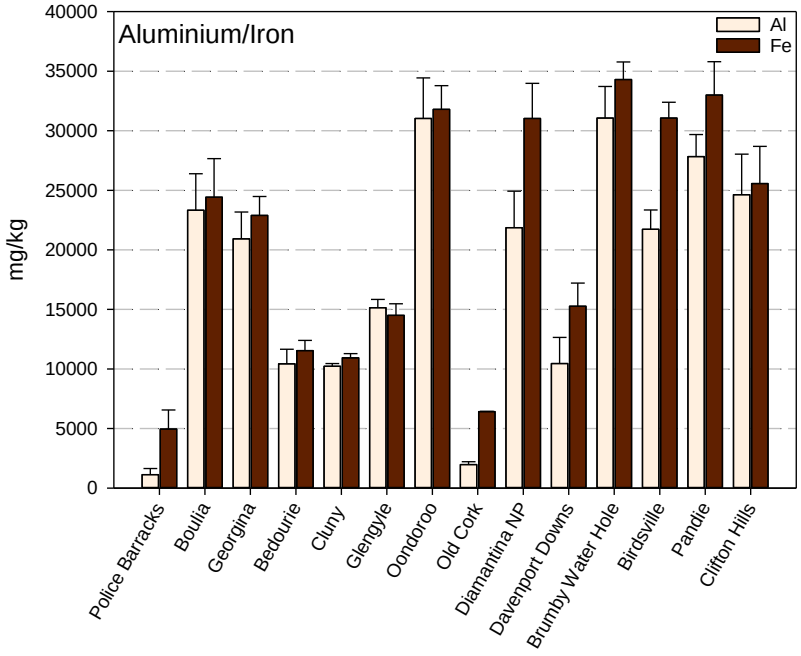

Figure A 19. Summary of Al and Fe in sediment samples

Appendix 7. Comparison physicochemical properties of collected soil, sediment and manure

Table A 3. Comparison of nutrient values obtained from soil, sediment and manure samples

Site	Matrix	C (%)	OC (%)	N (%)	NO_x-N, (mg/kg)	NH_4^+-N (mg/kg)	P (mg/kg)	PO_4-P (mg/kg)	Na (mg/kg)	K (mg/kg)	Ca (mg/kg)	Mg (mg/kg)
Police Barracks (Burke River)	Sediment	0.07±0.001	<0.01	<0.01	1.36±0.13	4.17±1.45	<100	3.87±0.3	<100	259±108	264±100	269±13
	Soil[a]	2.7	2.7	0.16	10	-	310	62	-	-	-	-
Boulia (Burke River)	Sediment	0.35±0.035	0.35±0.035	0.02±0.003	1.27±0.73	6.3±0.29	194±25	31.9±0.7	190±25	3390±445	3497±456	4053±5
	Soil	0.3	0.3	0.03	1.9	-	169	38	-	-	-	-
Georgina (Georgina River)	Sediment	0.38±0.05	0.36±0.07	0.03±0.01	2.85±1.1	11.9±1.9	207±7.6	23.4±1.4	128±11	3127±238	3570±193	3557±2
	Soil	0.4	0.4	0.04	29	-	190	53	-	-	-	-
Bedourie (Georgina River)	Sediment	0.23±0.04	0.21±0.05	<0.01	1.75±0.12	5.32±0.7	107±7.2	15.9±0.9	260±27	2023±198	2733±248	1903±1
	Soil	1.7	1.7	0.13	3.3	-	251	70	-	-	-	-
Cluny (King Creek)	Sediment	0.67±0.09	0.66±0.12	0.04±0.006	<1	17.12±0.75	128±2.1	23.3±0.6	184±23	1870±60	2507±204	1703±5
	Soil	0.6	0.6	0.06	14	-	206	59	-	-	-	-
Glengyle (Eyre Creek)	Sediment	1.17±0.15	0.35	0.02±0.003	1.64±0.18	8.26±0.07	193±9.71	33.8±0.4	112±5.3	2457±100	24067±1497	2970±1
	Soil	0.3	0.3	0.03	20	-	215	23	-	-	-	-
Oondoroo (Mills Creek)	Sediment	0.61±0.03	0.61±0.03	0.05±0.004	1.09±0.02	15.76±1.12	426±11	57.6±0.6	401±26	3473±309	7983±355	6290±4
	Soil	0.7	0.7	0.06	2.5	-	372	46	-	-	-	-
Old Cork (Diamantina River)	Sediment	0.01±0.001	<0.01	<0.01	1.52±0.3	3.19±0.11	<100	5.79±0.6	<100	300±28	600±49	439±4
	Soil	0.2	0.2	0.02	6.4	-	117	14	-	-	-	-
Diamantina NP (Diamantina River)	Sediment	0.57±0.08	0.57±0.08	0.04±0.006	1.02±0.23	20.69±1.07	310±31	59.4±2.5	202±16	1843±188	3743±344	2943±2
	Soil	0.4	0.4	0.03	2.9	-	177	30	-	-	-	-
Davenport Downs (Diamantina River)	Sediment	0.58±0.02	0.58±0.02	0.03±0.001	1.16±0.27	13.9±1.45	233±25	47.8±3.5	529±29	1270±198	2250±291	1730±2
	Soil	0.2	0.2	0.03	2.9	-	296	32	-	-	-	-
Brumby Waterhole (Diamantina River)	Sediment	0.51±0.12	0.51±0.12	0.03±0.003	<1	5.84±0.27	349±12	75.3±5	536±25	4697±258	4990±210	4993±2
	Soil	1.2	1.2	0.11	17	-	331	102	-	-	-	-
Birdsville (Diamantina River)	Sediment	0.51±0.06	0.51±0.06	0.04±0.005	<1	7.92±0.29	376±6	66.70±6	345±9.5	2963±71	4687±15	3777±1
	Soil	0.9	0.9	0.08	8.1	-	241	66	-	-	-	-
Pandie Pandie (Diamantina River)	Sediment	0.44±0.02	0.44±0.02	0.04±0.001	1.21±0.11	8.19±0.71	350±33	65.5±2.1	379±39	3987±430	5307±431	4707±4
	Soil	2.5	2.5	0.17	8.7	-	335	85	-	-	-	-
Clifton Hills (Diamantina River)	Sediment	0.62±0.13	0.62±0.13	0.04±0.006	1.69±0.17	6.18±0.37	302±41	75.3±12	305±37	3387±388	3983±556	3690±5
	Soil	1.2	1.2	0.11	35	-	588	129	-	-	-	-
All	Manure	31.6±12.4	-	1.57±0.64	-	-	3080±1752	-	1245±425	4507±1570	12573±4162	3565±6

[a]soil samples composited from around waterholes

Table A 4. Comparison of trace element values obtained from soil, sediment and manure samples

Site	Matrix	Al (mg/kg)	As (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Zn (mg/kg)
Police Barracks	Sediment	1128±510	14	<10	<10	4957±1592	32±14.1	<10	39±5.1
(Burke River)	Soil	15000	34	24	21	23300	334	13	31
Boulia	Sediment	23333±3061	27±4.5	25±3.5	19±2.5	24400±3200	393±54	13±1.8	35 ±2.9
(Burke River)	Soil	6900	22	20	12	18200	309	<10	29
Georgina	Sediment	20933±2254	27±2.6	33±16.4	17±2.5	22900±1580	327±24	11±0.9	18±1.9
(Georgina River)	Soil	19700	24	20	14	20000	311	11	33
Bedourie	Sediment	10433±1222	14±0.7	12±1.1	<10	11533±862	337±29	<10	18±1.9
(Georgina River)	Soil	15100	15	20	11	14200	171	<10	26
Cluny	Sediment	10223±225	13±1	12±0.1	<10	10933±351	75±3.2	<10	25±1.3
(King Creek)	Soil	16500	19	16	11	16500	262	<10	30
Glengyle	Sediment	15133±702	18±2.3	15±0.6	11±0.9	14500±964	179±13	<10	57±2.9
(Eyre Creek)	Soil	24700	27	17	16	23200	473	14	40
Oondoroo	Sediment	31033±3403	38±1.2	22±1.9	18±0.4	31800±1992	576±25	15±0.6	<10
(Mills Creek)	Soil	22200	31	23	11	22300	479	11	40
Old Cork	Sediment	1970±236	12±0.6	<10	<10	6420±17	121±15	<10	46±5.9
(Diamantina River)	Soil	10700	20	16	<10	15100	369	<10	23
Diamantina NP	Sediment	21866±3066	44±3.7	22.4±2.3	22±5.9	31033±2948	716±109	12±1.4	25±2.9
(Diamantina River)	Soil	10600	23	13	<10	16300	568	<10	25
Davenport Downs	Sediment	10450±2196	22±1.9	13±1.7	11±0.9	15267±1950	336±40	<10	59±2.5
(Diamantina River)	Soil	15400	33	14	12	21800	508	<10	35
Brumby Waterhole	Sediment	31066±2657	39±1.9	27±1.6	21±0.9	34300±1473	672±16	16±0.6	109±54
(Diamantina River)	Soil	18500	19	17	11	17900	340	<10	34
Birdsville	Sediment	21733±1625	44±1.6	22±1.4	157±127	31067±1331	911±36	14±0.2	57±5.7
(Diamantina River)	Soil	19800	23	16	12	20000	309	<10	45
Pandie Pandie	Sediment	27833±1850	42±5.2	25±2.2	23±4	33000±2800	734±81	16±1.5	44±5.6
(Diamantina River)	Soil	23100	27	17	16	24800	448	12	45
Clifton Hills	Sediment	2463±3412	30±4.4	22±2.7	17±2.3	25567±3126	459±56	12±1.8	39±5.7
(Diamantina River)	Soil	14300	17	20	<10	15100	259	<10	30
All	Manure	7302±4510	6.64	4.99±2.87	13.85±2.2	5480±4337	162±60	4.44±1.94	55.3±4.9

Appendix 8. Excitation-emission fluorescence spectra of fDOC at each site

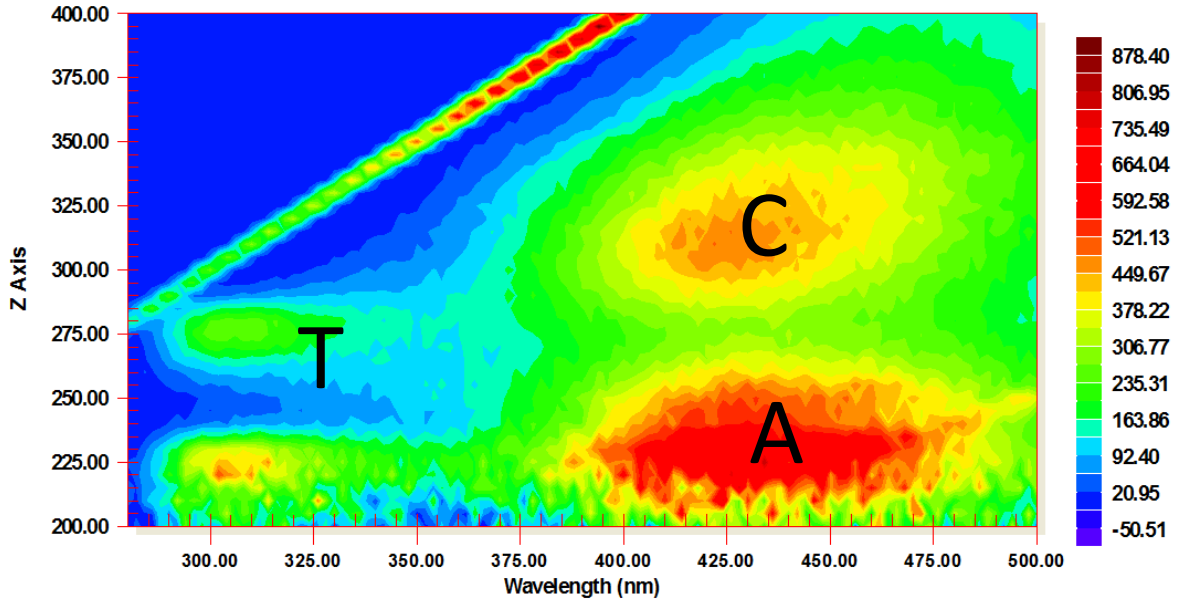

Figure A 20. Fluorescence spectrum for ultrapure water extract of manure (pooled from all sites) covering entire excitation (Z axis) and emission (X axis) range of wavelengths. Region A and C relate to humic and fulvic-like, plant-derived DOC fluorescence, while region T relates to tryptophan-like, microbially derived DOC.

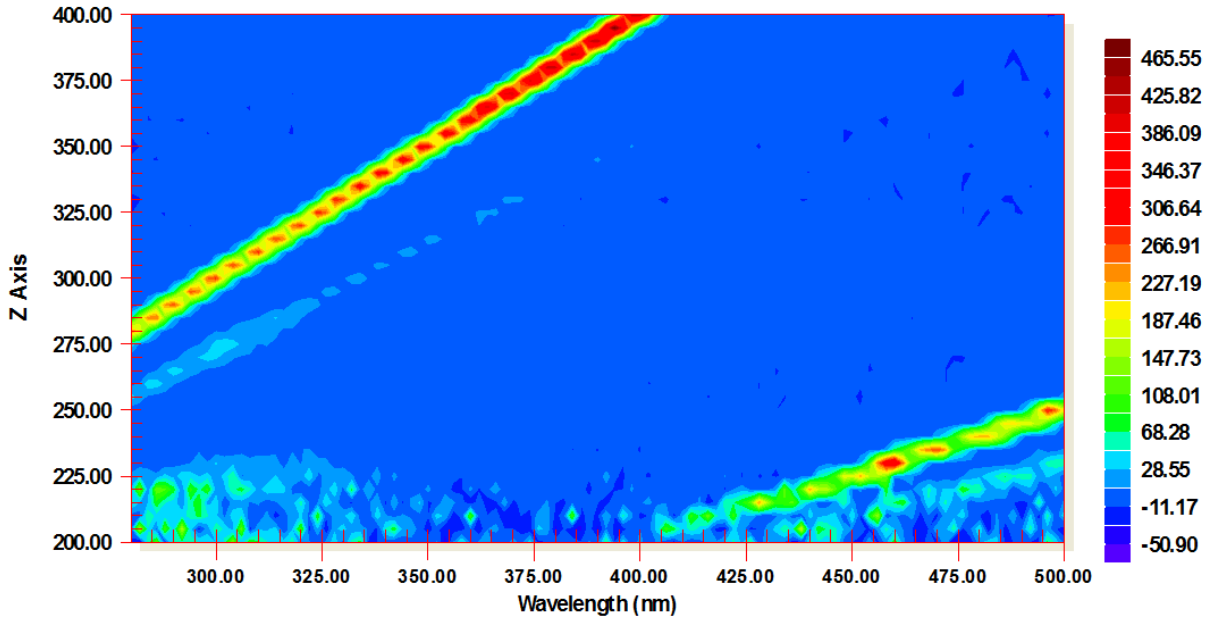

Figure A 21. Fluorescence spectrum for ultrapure water covering the entire excitation (Z axis) and emission (X axis) range of wavelengths

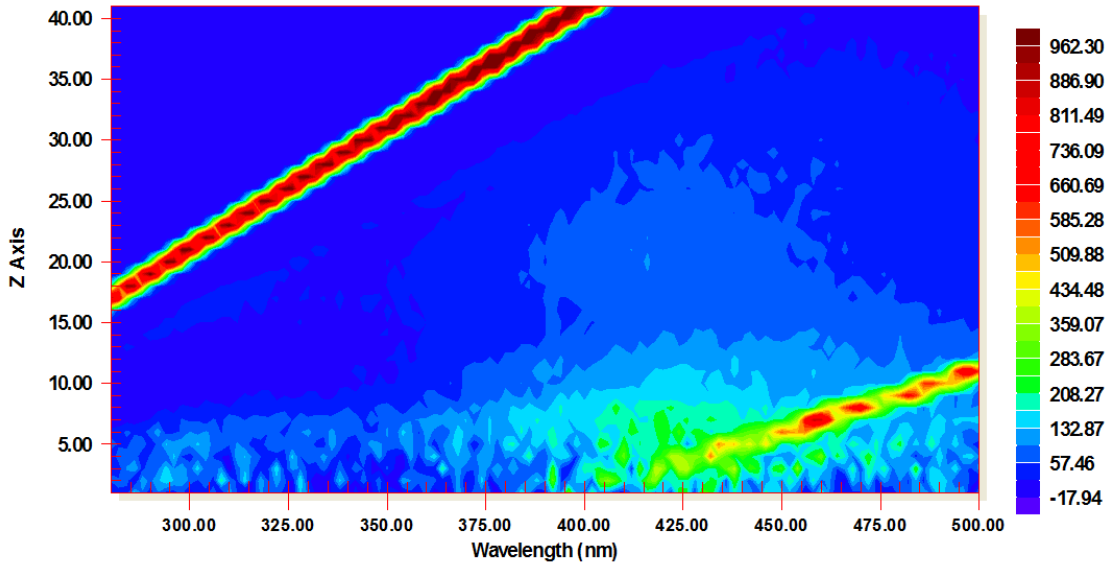

Figure A 22. Fluorescence spectrum for water collected from the Police Barracks (Burke River), covering the entire excitation (Z axis) and emission (X axis) range of wavelengths

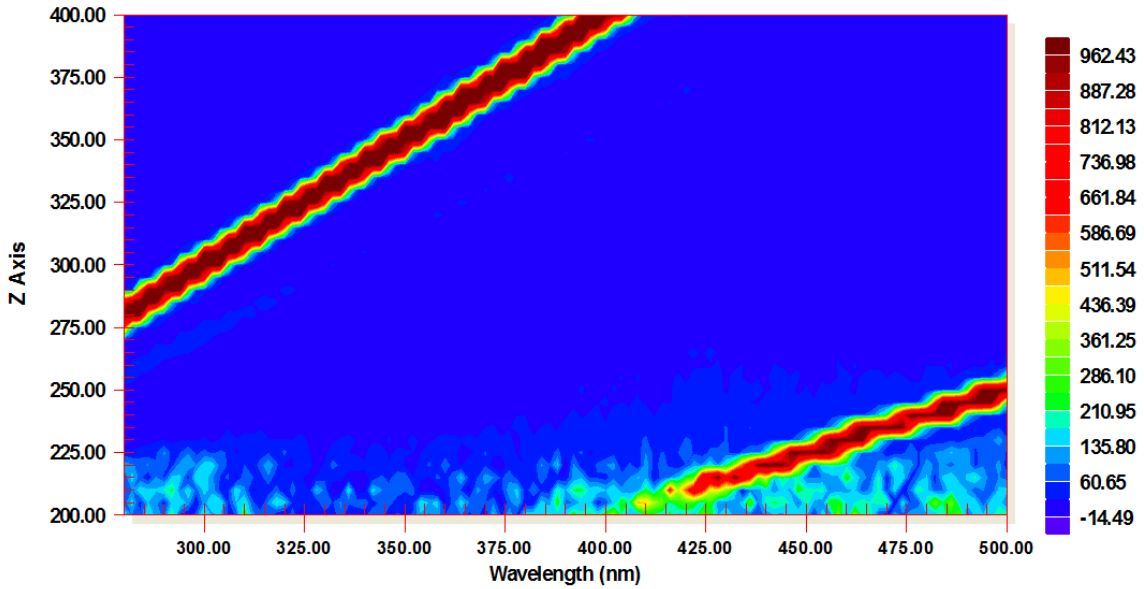

Figure A 23. Fluorescence spectrum for water collected from the Boulia (Burke River), covering the entire excitation (Z axis) and emission (X axis) range of wavelengths

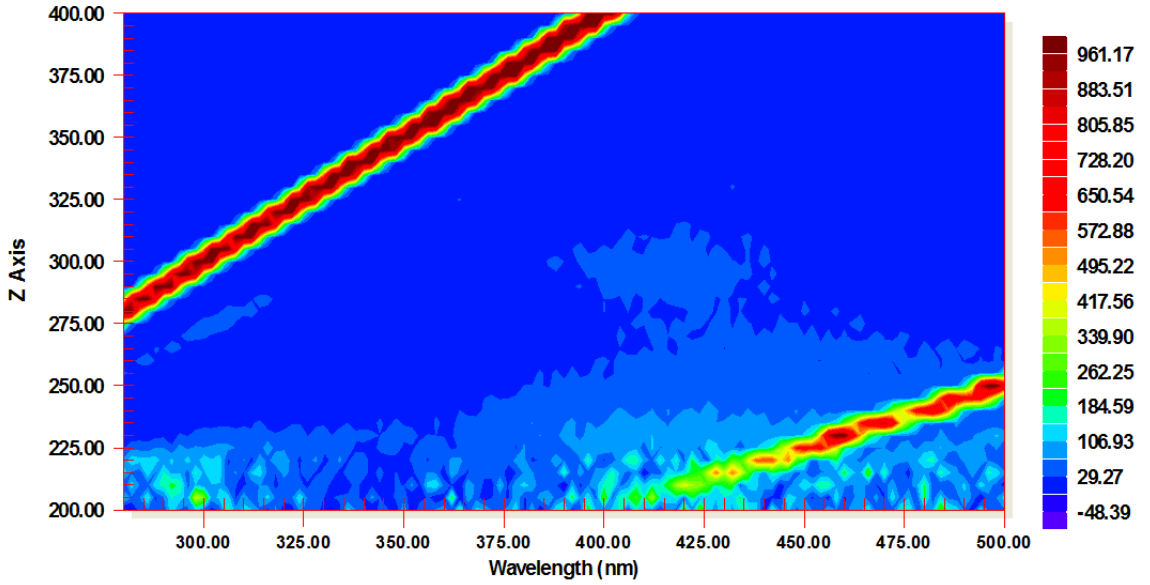

Figure A 24. Fluorescence spectrum for water collected from the Georgina (Georgina River), covering the entire excitation (Z axis) and emission (X axis) range of wavelengths

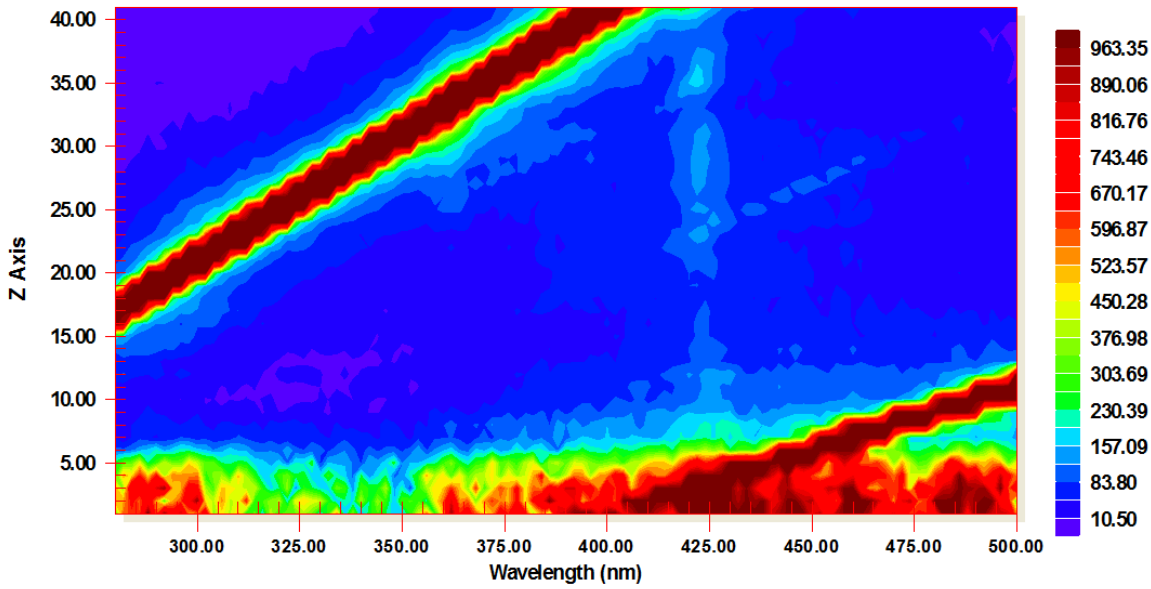

Figure A 25. Fluorescence spectrum for water collected from the Bedourie (Georgina River), covering the entire excitation (Z axis) and emission (X axis) range of wavelengths

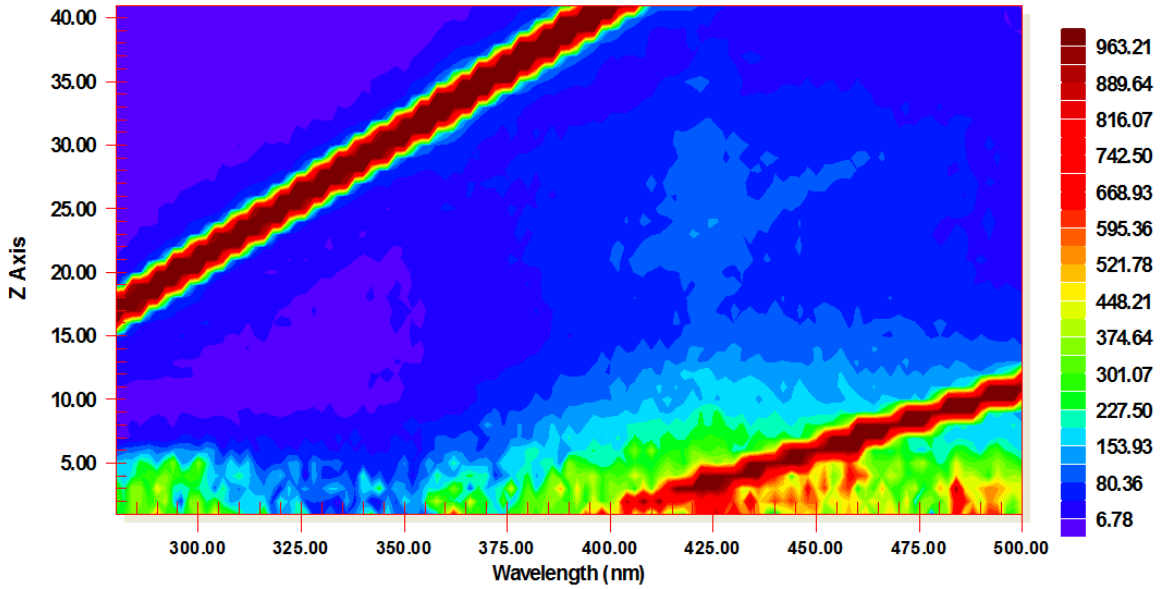

Figure A 26. Fluorescence spectrum for water collected from the Glengyle (Eyre Creek), covering the entire excitation (Z axis) and emission (X axis) range of wavelengths

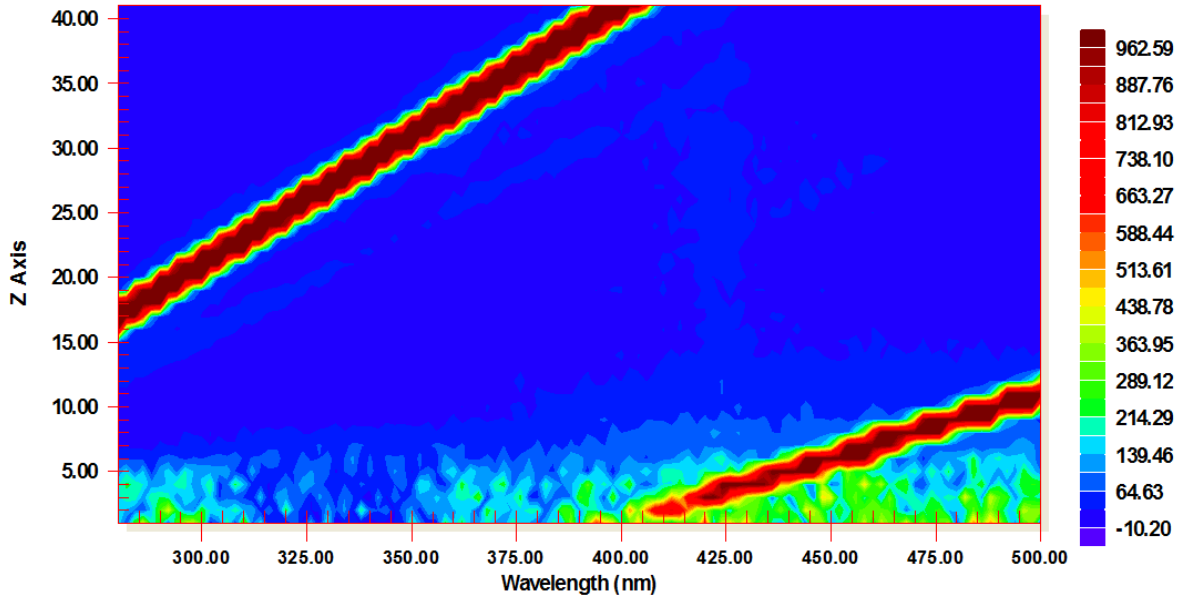

Figure A 27. Fluorescence spectrum for water collected from the Oondoroo (Mills Creek), covering the entire excitation (Z axis) and emission (X axis) range of wavelengths

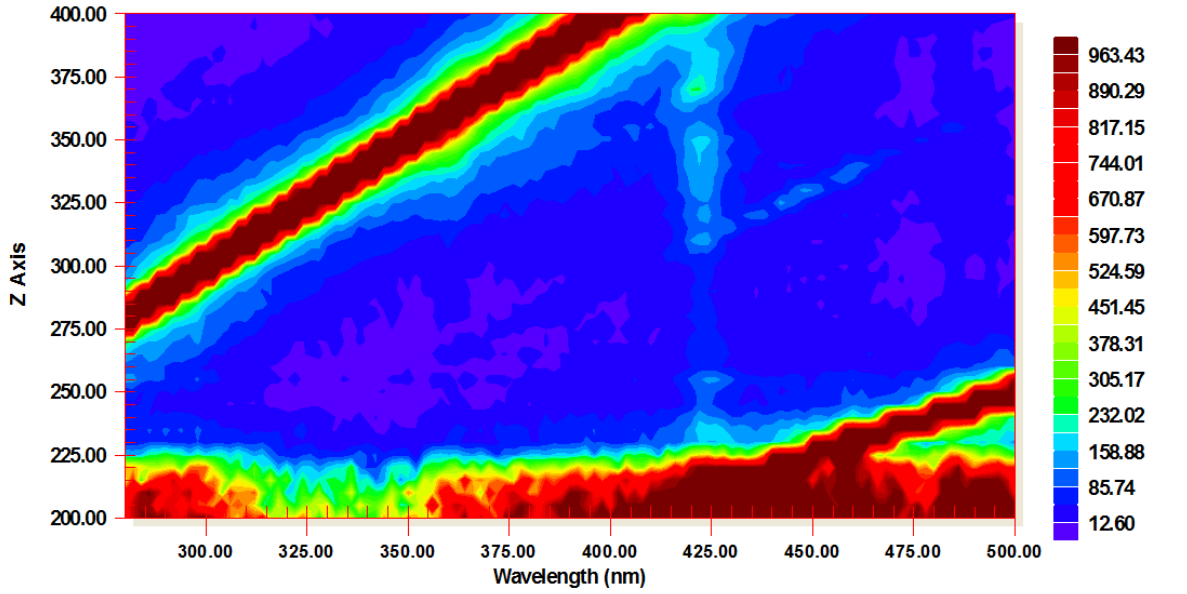

Figure A 28. Fluorescence spectrum for water collected from the Old Cork (Diamantina), covering the entire excitation (Z axis) and emission (X axis) range of wavelengths

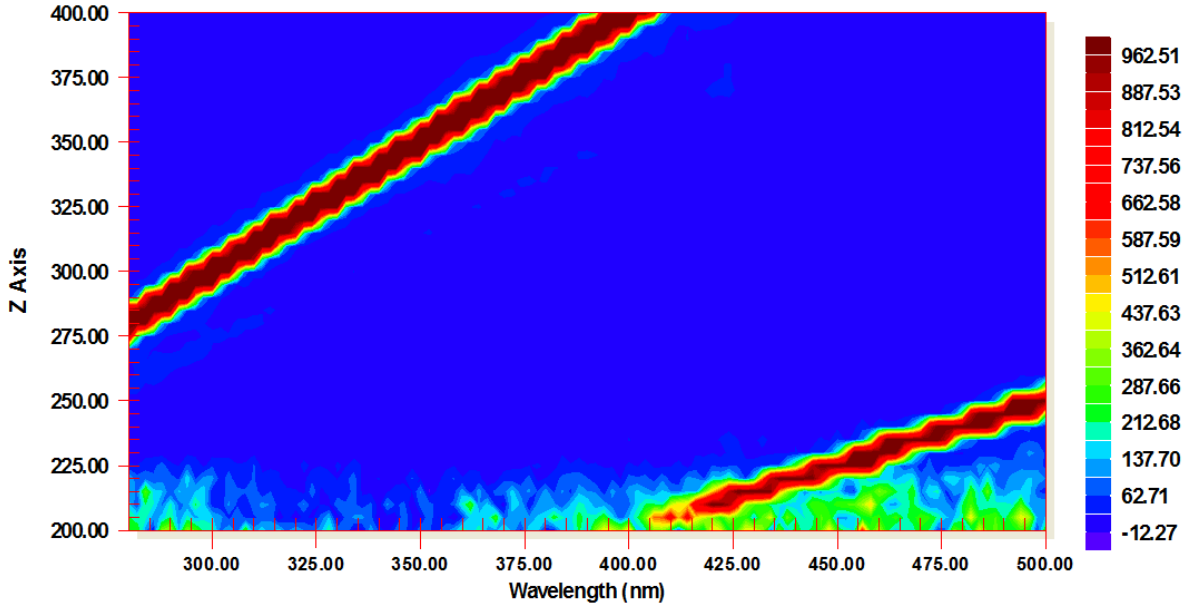

Figure A 29. Fluorescence spectrum for water collected from the Diamantina NP (Diamantina River), covering the entire excitation (Z axis) and emission (X axis) range of wavelengths

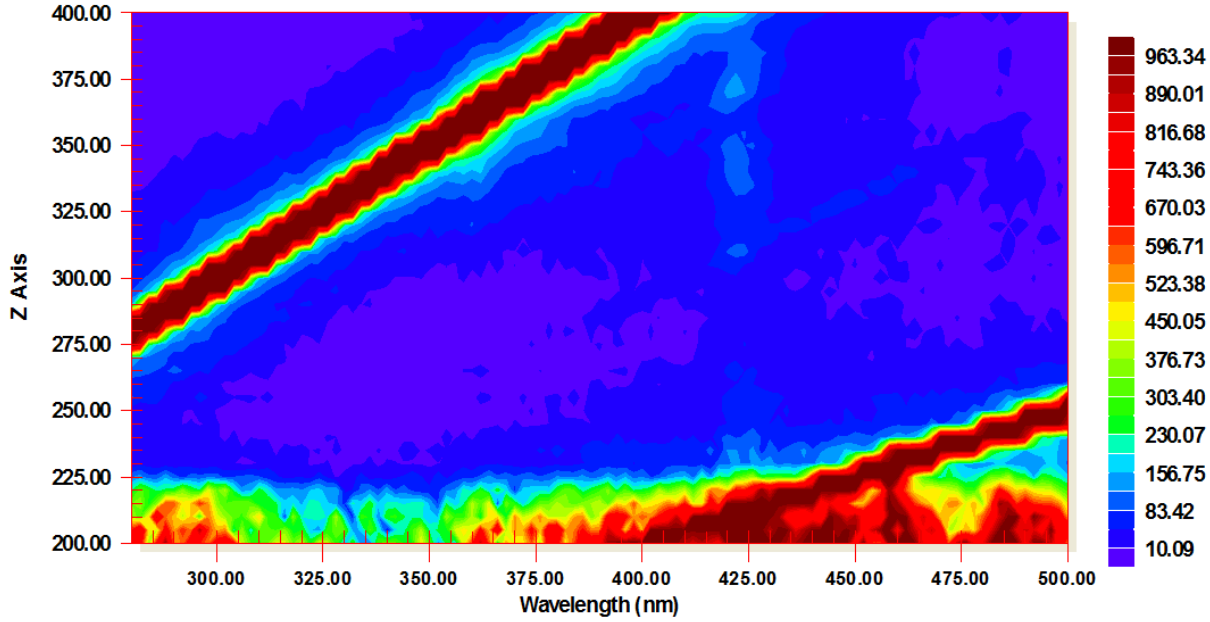

Figure A 30. Fluorescence spectrum for water collected from the Davenport Downs (Diamantina River), covering the entire excitation (Z axis) and emission (X axis) range of wavelengths

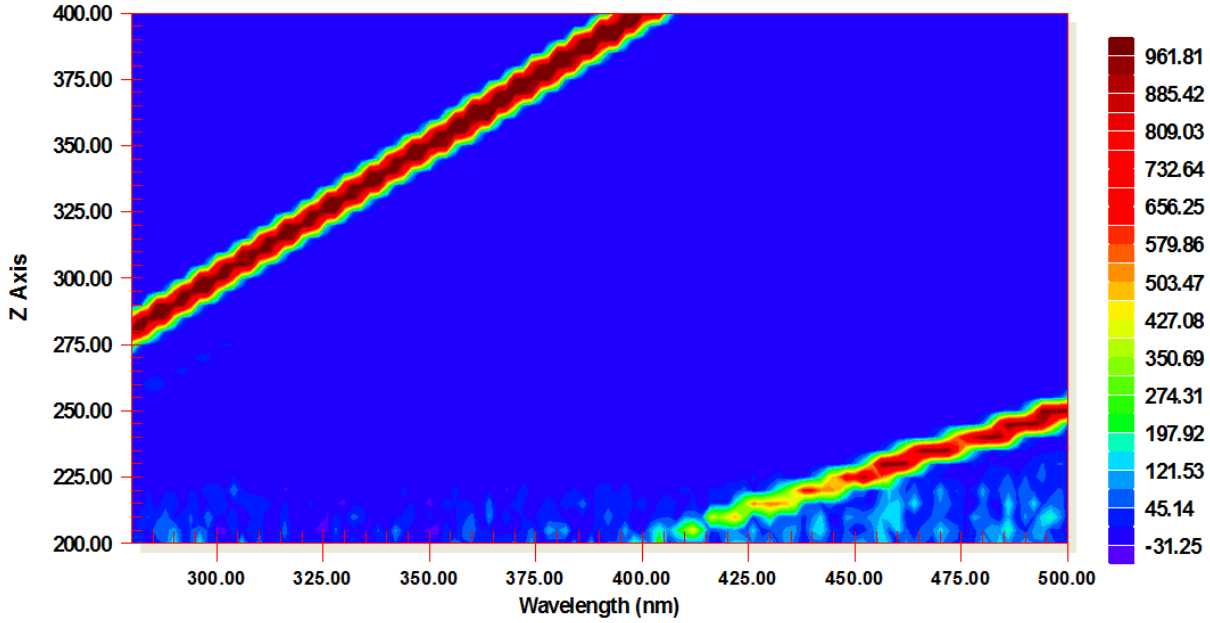

Figure A 31. Fluorescence spectrum for water collected from the Brumby Waterhole (Diamantina River), covering the entire excitation (Z axis) and emission (X axis) range of wavelengths

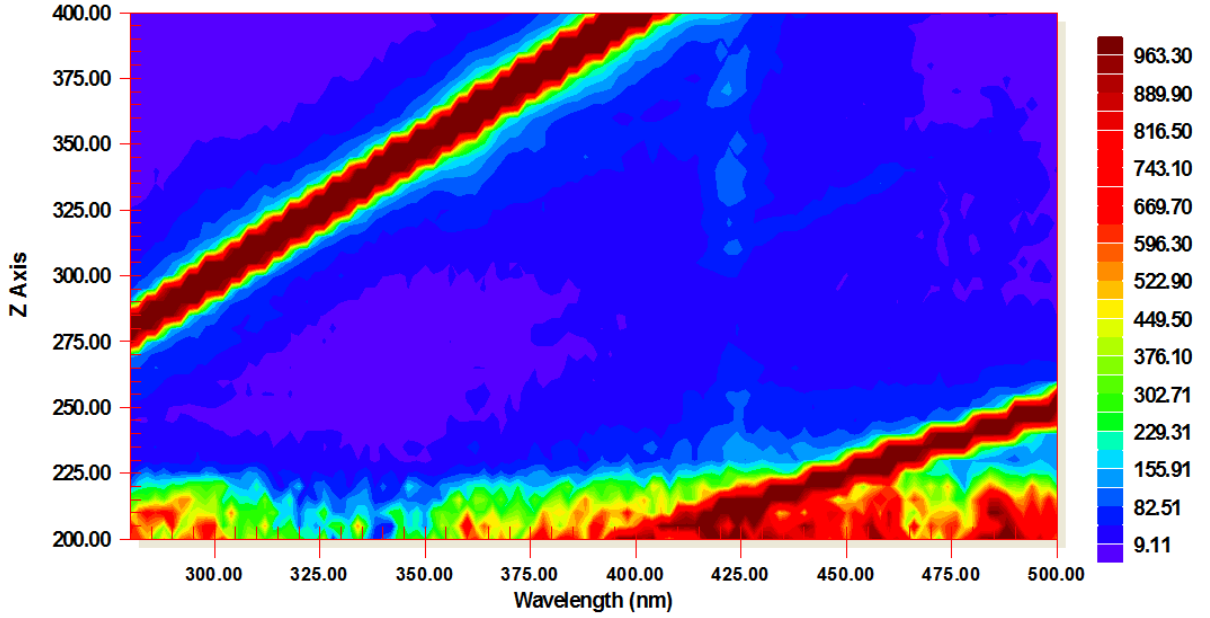

Figure A 32. Fluorescence spectrum for water collected from the Birdsville (Diamantina River), covering the entire excitation (Z axis) and emission (X axis) range of wavelengths

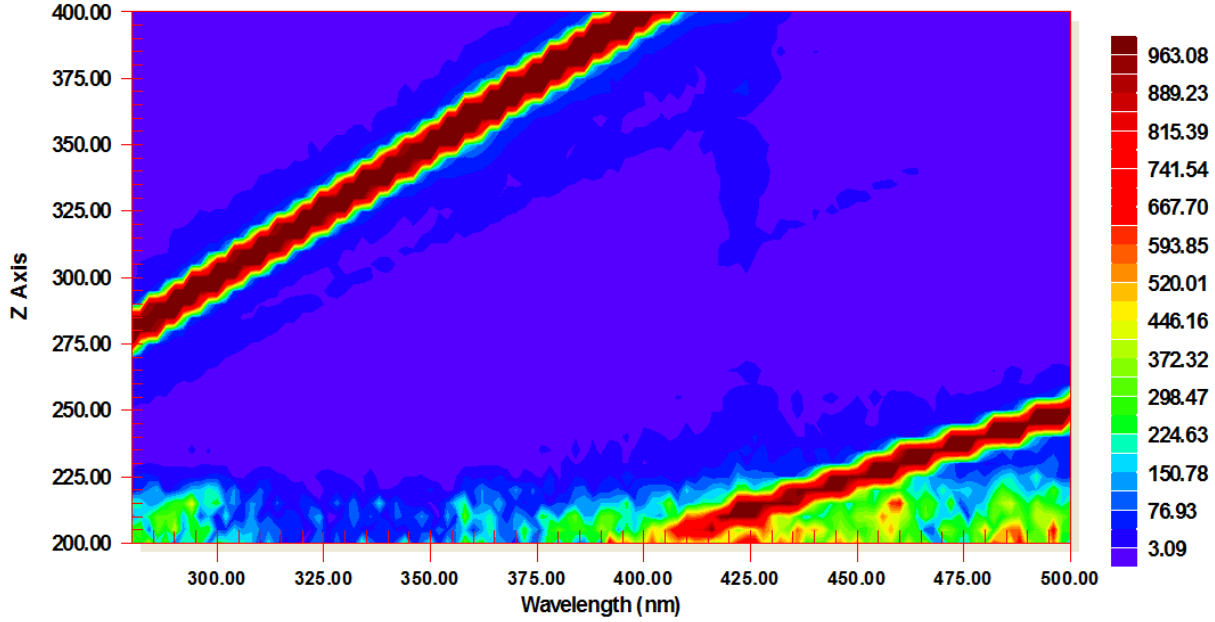

Figure A 33. Fluorescence spectrum for water collected from the Pandie Pandie (Diamantina River), covering the entire excitation (Z axis) and emission (X axis) range of wavelengths

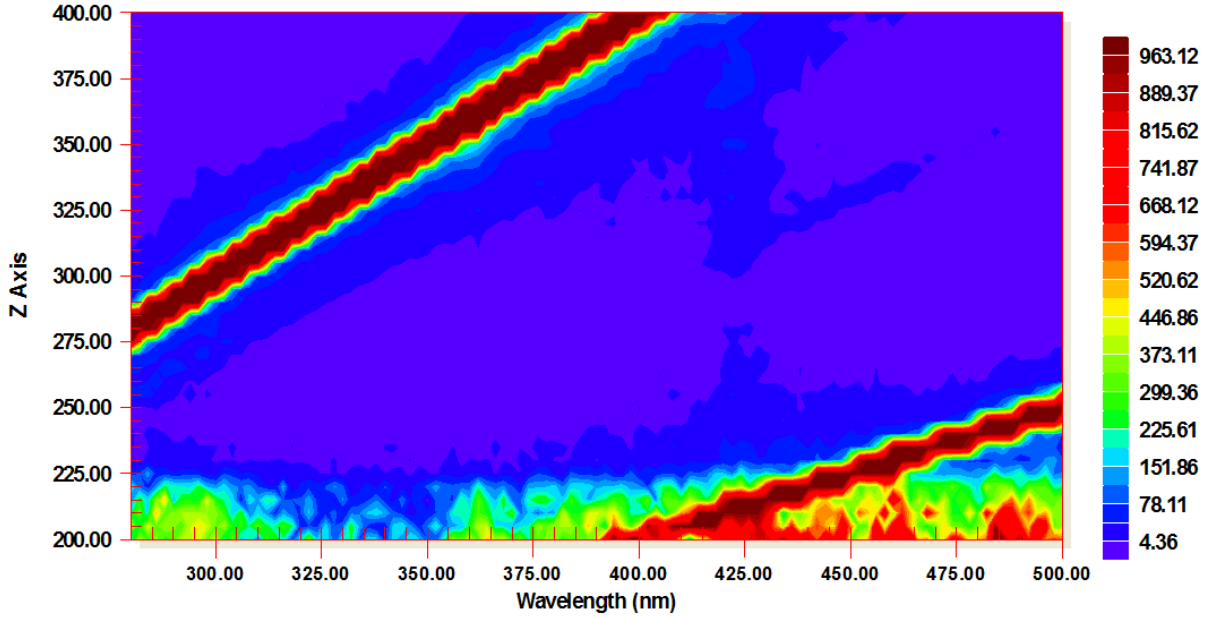

Figure A 34. Fluorescence spectrum for water collected from the Clifton Hills (Diamantina River), covering the entire excitation (Z axis) and emission (X axis) range of wavelengths

Appendix 9. Apportionment of nutrient sources in the Lake Eyre Basin – strategies for identifying and monitoring anthropogenic inputs

Tracking pollution sources

Many markers have been used to track contamination sources with varying degrees of success. These include isotopic elemental markers (e.g. N, O, B, U); dissolved organic carbon (especially protein like compounds with fluorescent properties); sewage-associated trace organic compounds (e.g. pharmaceuticals, hormones, artificial sweeteners), markers used microbial source tracking (MST) to discriminate between human and non-human sources and also to track specific animal sources; phytoplankton and molecular organic proxies used mainly for condition assessment of waterways. The requirements for robust markers need to be source-specific and consistent with the contaminant sources, conservative during their transport in the environment and that these can be analysed with sufficient sensitively and repeatability (Badruzzaman et al. 2012). Here, we provide a literature review of different classes of markers together with their strengths and weaknesses, especially in the context of dominant land uses in LEB. We have also identified the markers that may or may not be suitable for application in the LEB.

Isotopes as tracers

Isotopes of trace elements have been used for identifying sources of nutrients in surface water and ground waters over last 20 years (e.g. Kendall, 1998; Katz et al. 1999; Kendall and Aravena, 2000). Some of the promising elemental isotopic markers of potential use have been compiled by Badruzzaman et al. (2012). These include nitrogen, oxygen, boron, uranium, strontium and carbon. These isotopes have been used to identify various natural and anthropogenic nutrient sources but also subject to confounding factors leading to enrichment during their transport.

Enrichment of $\delta^{15}N$ values in dissolved inorganic nitrogen (DIN) has been suggested to indicate the human or animal wastes as sources of nitrogen (Kendall 1998). However, processes such as denitrification (especially during wastewater treatment) and ammonia volatilisation (e.g. from animal manures) can also result in enrichment of ^{15}N and thus may confound the interpretation (Fertig et al. 2013). According to Kendall (1998), the $\delta^{15}N$ values of DIN that has not been denitrified has values for NO_3^- and NH_4^+ ranging from -4 to +4‰ (parts per thousand).

Pinpointing of sources of elevated $\delta^{15}N$ in catchments that are intermediate stage of development may be difficult as compared to those catchments that are highly developed (Fertig et al. 2013). For example, Fertig et al. (2013) reported that while the elevated $\delta^{15}N$ in Delaware Island Bays could be clearly linked to the anthropogenic sources in their highly developed catchments, the identification of sources through this approach was difficult in the Johnson Bay (Maryland-Virginia, USA) associated with intermediate level of development. Considering that the Lake Eyre Basin has very little development, the $\delta^{15}N$ approach may have limited discriminatory capability in terms of sources.

Markers for microbial source tracking

A range of microbial markers have been used microbial source tracking (MST) to discriminate between human and non-human sources and also to discriminate between specific animal sources e.g. concentrated animal feeding operations (CAFOs). These include faecal indicator bacteria (FIB) or animal specific microbial markers, the former being non-specific to sources and can originate from multiple sources such as human sewage, animal manure, wildlife, urban runoff (Boehm et al. 2013). In recent years, genetic biomarkers associated with particular animal faeces have become attractive tools of MST. Other MST methods include viruses specific to human faecal wastes, chemical, community-based and metagenomics methods (Boehm et al. 2013).

In terms of animal specific MST markers, a recent study Heaney et al. (2015) used faecal coliforms, *E. coli* and *Enterococcus* as well as swine-specific microbial source-tracking markers namely *Bacteroidales* Pig-1-bac; Pig-2-Bac, Pig-Bac-2 and methanogen P23-2. Based on a study on a total of 187 samples collected weekly over six months from swine farming sites in eastern North Carolina, they noted that Pig-1-bac; Pig-2-Bac were 2.47 and 2.30 times more prevalent at downstream sites than the upstream sites of CAFOs. They concluded that the Pig-1-bac; Pig-2-Bac are useful markers for tracking the distribution of swine faecal wastes. Quantitative PCR studies combined with the above could have been more powerful approach.

Performance of MST methods was evaluated by Boehm et al. (2013) in an inter-laboratory study involving 27 different laboratories and 41 MST methods. This study identified a range of specific and sensitive assays covering human, and various animal-specific sources including cows, pigs, chicken, horse and other animals. The top performing assays were for Humans - HF 183; for ruminants - CF 1 and Rum2Bac; for cows – CowM2 and Cow M3; for pigs – pigmtDNA; for horse – HoF597 (Boehm et al. 2013). The survey also highlighted several issues including inter-laboratory variability, inconsistent data analysis and interpretations and matrix interferences. Further work such as to understand matrix effects on nucleic acid extraction recovery and PCR inhabitation was recommended.

Faecal materials from wildlife or animals can remain dry in catchments for weeks before it is washed into water bodies and this can be a real challenge in data interpretation, particularly when different MST markers breakdown at differential rates (Stewart et al. 2013). This is particularly relevant for the conditions in the Lake Eyre Basin where MST markers from animal sources may be impacted during the release and transport phases.

Dissolved organic carbon

Dissolved organic matter (DOC) is ubiquitous constituent of water in waterways. It is well established that both the concentrations and the chemistry of DOC is influenced by the source and landscape influences (Hedges et al. 1980) and therefore there has been interest in using this as a tracer to link the pollution with the land use. However, due to the relatively rapid transformations in DOC during the transport to and in the water body, the specificity of DOC as a marker diminishes. Furthermore, often the complexity of land covers also makes the interpretation difficult.
It is generally believed that low molecular weight (MW) fraction is preferentially degraded by microorganisms in riverine ecosystems and the high MW fraction being recalcitrant accumulates in the receiving environment. However, the latter is more likely to be retained in soil or sediments.
In a study that collected stormwater samples during runoff events at the terrestrial-aquatic interface from catchments associated with single land use in urban and suburban areas, McElmurry et al. (2014) observed that forested land produced high MW DOC (due to plant exudates), with high aromaticity and a large range of polydispersivity, whereas those the paved surfaces in urban and

suburban areas produced DOC with low MW, lower aromaticity and higher hydrophobicity (possibly reflecting the contribution of petroleum hydrocarbons). The areas drained by storm sewers was also found to be more hydrophobic than other areas. They also suggested that isotopic analysis can assist in the identification of age of DOC pools.

Fluorescence spectroscopy

DOC can absorb certain wavelength of light and re-emit a fraction of that energy as fluorescence. This led to the development of fluorescence spectroscopy as a method to quantify and characterise a subset of DOC pool in water (Coble 1996). The characteristic fluorescent spectral difference between natural DOC such as humic acid type, from the DOC originating from sewage or wastewaters (protein-like) have been harnessed to trace the source of pollution, especially in sewage impacted waters (Henderson et al. 2009). Indeed, optical techniques such as UV-absorbance and fluorescence spectroscopy has been used for monitoring of wastewater treatment processes for quite some time (Hudson et al. 2007), however, the latter is 10-1000 times more sensitive and therefore more attractive (Henderson et al. 2009).

The technique has been facilitated by the emergence of rapid detection of three-dimensional excitation-emission matrices (EEM), as a composite of emission scans obtained from an array of wavelengths, as shown in the figure below. The EEMs from river water where the humic-like peaks (A & C) are observably different from the tryptophan type peaks (T1 and T2) which dominates the raw sewage. However matrix interferences such as due to the presence of metal ions, and pH and temperature variations can affect the peak intensities. The T1 and T2 peaks have been found to be strongly correlated with BOD, PO_4^{3-}; NO_3^-.and to a lesser extent with NH_3 and COD (Henderson et al. 2009).

EEM spectroscopy has been applied in a number of studies for tracking and characterization of wastewater in rivers (Hudson et al. 2007). Hambly et al. (2010) applied the EEM spectroscopy technique at three Australian sites that were connected to dual distribution system (i.e. drinking and recycled water). Over a period of 12 weeks the authors compared the EEM spectroscopy technique to assess its discriminating power between recyclable and potable water. They found that the comparison of T peak ($\lambda_{ex/em}$ = 300/350 nm) with the A peak ($\lambda_{ex/em}$ = 235/426 nm) the three recycled water could be differentiated. While the electrical conductivity was 5 times different between the potable and recycled water, the T peaks were 10 times different. On this basis the authors concluded the EEM spectroscopy as a promising tool. More recently, Goldman et al. (2012) applied the above technique together with statistical approaches (end-member - EM - mixing models, multivariate linear regression- MLR) to an urbanised part of the river basin (Tualitin River) in USA, and could predict the percentage of wastewater in river water samples with 80% confidence (Figure xx). They found that EM models based separately on peaks A, T or C did not perform well and overestimated the percent wastewater in samples. Among these peaks, peak T was found to be somewhat better predictor but its accuracy was compromised due to mixture of DOC from multiple sources. Variants of the above technique has also been found to be promising in detecting differences in DOC originating from industrial wastewaters from different industrial sources. For example, Li et al. (2014) found that humic-like substance with triple excitation peaks (($\lambda_{ex/em}$= 250,310,365/460 nm), possibly 1-amino 2-napthol, an intermediate compound of azo dyes, could be used as a specific fluorescence indicator of textile effluents. However, recent work highlighted some challenges in broad application of the technique to a wide variety of industrial effluents (Yang et al. 2015).

Trace organic compounds as wastewater markers

Advancements in analytical chemistry have enabled sensitive detection of trace concentrations of a range of organic compounds derived from wastewater (commonly referred to as micropollutants). Since many of these are not sufficiently removed during the wastewater treatment process, a range of compounds have been commonly detected in treated wastewaters. These include artificial sweeteners (sucralose, aspartame) pharmaceuticals (e.g. antiepileptics, NSAIDS, lipid-lowering drugs), plasticizers (BPA), alkyphenols (surfactant metabolites such as nonylphenols, octylphenols), stimulants (e.g. caffeine), animal steroids (coprostanol), plant steroids, insect repellents (DEET), polycyclic musks, anticorrosion agents (benzotriazoles), chelating agents (Badruzzaman et al. 2012).

So far the most promising markers of wastewaters include carbamazepine (pharmaceutical); acesulfame, sucralose (artificial sweeteners), galaxolide (synthetic musk), gadolinium anomaly (chelating agent used for X-ray contrast). While gadolinium is a very sensitive marker, it is more suitable for urban centres where likelihood of its use and release in the waste stream are high and vice versa. It is therefore unlikely to be of much value in the Lake Eyre Basin.

Phytoplankton and molecular organic proxies

Phytoplankton including cyanobacteria play important roles in C, N, Fe and S cycling in aquatic ecosystems. In Australia, Bunn and Davis (1999) found that the most important source of C for consumers was from primary producers in permanent waterholes in the Lake Eyre Basin. Diatoms, due to their ubiquitous presence in various aquatic habitats and being easy to use, are commonly monitored as indicators of contamination and nutrient enrichment in riverine and lacustrine environments.

Diatom indices have been developed and used to monitor pollution of streams in several countries (e.g. Watanabe et al. 1988; Van Dam et al. 1994; Whitton and Rott, 1996). A working party on river health assessment in semi-arid and arid rivers in Australia (Environment Australia 2000) recommended diatoms as a useful tool in the Australian Rivers Assessment Scheme (AusRivAs) toolbox. Diatoms can be used as indicator of water quality and are recommended to be used together with fish, macro invertebrates or vegetation monitoring.

Studying the impact of urban pollution on benthic diatom communities of three rivers of Vietnam, Duong et al. (2006) found a correlation between diatom assemblages and water quality parameters. Two diatom indices showed congruence and were associated with highly polluted river receiving pollution from multiple sources. However, identification of specific source of contamination was beyond the scope of the study.

Molecular organic proxies associated with algae, diatoms, microbes and higher plants living on land or in water are used to construct past environmental conditions in lacustrine environments (Castaneda and Schouten, 2011). A range of molecular organic proxies can be used as biomarkers arising from organisms in land and water as well as from different sources. Modern analytical methods such as HPLC/MS and compound specific isotope analysis have identified a broad range of molecular organic proxies. While, Castaneda and Schouten (2011) discussed in detail, the potential utility of various biomarkers in paleo-environmental reconstruction of lacustrine environment and also for the input of terrestrial organic matter into freshwater ecosystem. However, their utility in contaminant source tracking is not clear.

Need for multiple tracers

Many studies tend to use a single type of tracer to identify anthropogenic inputs into receiving environments; however, contaminant sources are often complex and this approach may be inadequate. Essentially, all specific tracers have relative advantages and disadvantages. For example, while for wastewater sources EC is a relatively simple parameter that can be measured on-line and cost effectively (Ort and Siegrist, 2009), it is non-specific and may be rendered ineffective in receiving environments with high background EC levels, e.g. waterways in arid regions or estuaries. In contrast, a tracer such as pharmaceuticals is specific to human sewage input, but the cost of sample preparation and analysis can be high and the trace levels present in the source may be diluted rapidly in the receiving environments making it undetectable. Multiple tracers, ideally both specific and sensitive, together may provide much better chances of tracking pollution sources.

Williams et al. (2013) compared four tracers commonly found in wastewater effluents, namely, the human pharmaceutical carbamazepine (CBZ), anthropogenic gadolinium (Gd), fluorescent dissolved organic matter (fDOC) and electrical conductivity, in their relative effectiveness in determining the extent of sewage effluent in freshwater systems. While EC and fDOC were non-specific tracers to indicate relative input to wastewater in the receiving environment, the other two, CBZ and Gd, were specific to human use only. CBZ is used primarily as a therapeutic agent to treat epilepsy, while the anthropogenic Gd anomaly is as a result of its use as an organometallic MRI contrast agent. They applied these tracers to two distinct freshwater systems receiving wastewater effluents; one with a high level of effluent dilution (effluent <1% of total flow), and the other with a low level of effluent dilution (effluent ~50% of total flow). They found that while at both sites the selected tracers exhibited a similar pattern of response downstream of discharge points, they recommended that combining the tracers that are specific to a source (e.g. CBZ or Gd together with easy to use non-specific tracers (e.g. EC or fDOC) are likely to provide a more robust means of delineating the wastewater influence in receiving environments.

Table A 5. Summary of source trackers and their suitability for use within LEB

Chemical class	Specific compounds	Strength	Weakness	Suitability for the Lake Eyre Basin
Artificial sweeteners	Sucralose, acesulfame, aspartame	Several compounds are highly persistent and mobile	Human consumption related marker only	Not suitable as humans are not expected to be a major source of pollution
Animal/human hormones	17α estradiol 17β estradiol estrone	Some compounds are specific to animal sources	May breakdown in environment Concentrations may be low.	Potentially useful
Isotopic elements	$\delta^{11}B$; $\delta^{15}N$ & $\delta^{18}O$; $^{87}Sr/^{86}Sr$; $^{234}U/^{238}U$	Sewage effluent marker; Fertiliser vs sewage N; Indicative of fertiliser N; Indicative of fertiliser N	-- Inconclusive Non-specific Non-specific	Not suitable
Gadolinium	Gd	Very specific to human source; also sensitive	Need large population base	Not suitable
Microbial source tracking markers	HF 183 (Humans); F 1 and Rum2Bac (ruminants); CowM2 and Cow M3 (cattle); pigmtDNA (pigs); HoF597 (horse)	Specific to a particular source and sensitive (see table xx) Validated by inter-laboratory comparisons	Local capability and testing	Highly suitable, especially with cattle grazing as the dominant land use in the basin
Stimulants	Caffeine	Widespread use and ubiquitous	Not sufficiently conservative, breaks down Nonspecific to wastewater	Not suitable, except in specific hotspots of tourism activities
Pharmaceuticals and other organic compounds associated with sewage	Carbamazepine	A conservative and mobile tracer that is commonly detected in sewage impacted environments;	A small population may not provide sufficient signal	Not suitable, as there is unlikely to be major source of sewage impact in LEB
Dissolved organic matter	Fluorescent DOC	Useful in sewage impacted system	May not be sensitive enough	Potentially useful
Phytoplanktons	Diatoms	Good indicators of pollution and condition assessment	Non-specific; Source tracking may be difficult	Potential useful in condition assessment, similar to other measures such as macroinvertebrates and fish
Molecular organic proxies	e.g. C_{29} n-alkane and Vanillic acid	Specific to terrestrial higher plants	Not widely used; analytical cost may be high	Not suitable

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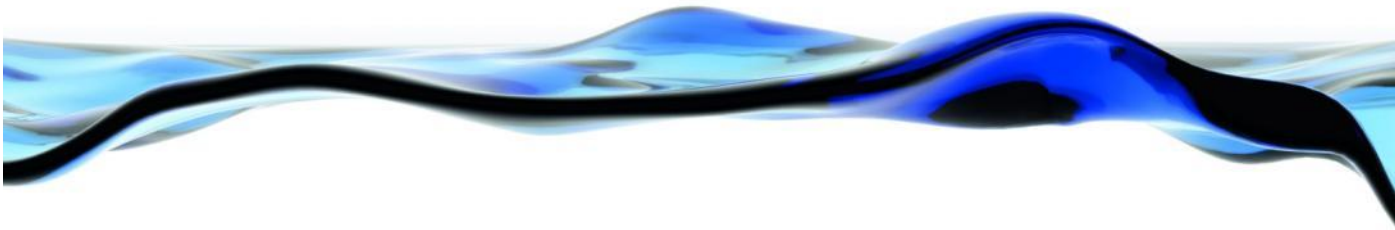

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