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Water quality in two Australian dryland rivers: spatial and temporal variability and the role of flow

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Abstract

Water quality, along with hydrology, plays an important role in the spatial and temporal dynamics of a range of ecological patterns and processes in large rivers and is also often a key component of river health assessments. Geology and land-use are significant drivers of water quality during flow periods while during periods of no-flow, local-scale factors such as evaporation, groundwater influence, and the concentration and precipitation of compounds are important. This study explored the water quality changes in two Australian dryland rivers, the Cooper Creek, Lake Eyre Basin, and the Warrego River, Murray-Darling Basin, across different hydrological phases over a number of years. Water quality varied both spatially and temporally; the greatest spatial variability occurred during the no-flow phase, with temporal changes driven by flow. Concentrations of major anions and cations also varied spatially and temporally, with an overall cation dominance of calcium and magnesium and an anion dominance of bicarbonate. This bicarbonate dominance contrasts with previous data from inland lentic systems where sodium chloride was found to dominate. Such extreme spatial and temporal variability hampers successful derivation of water quality guidelines for these variable rivers and suggests such guidelines would need to be developed with respect to ‘flow phase’.

Keywords: water quality guidelines, ionic chemistry, variability, hydrology

Introduction

In regions with hyper-arid, arid, semi-arid and dry-subhumid climates, the conversion of rainfall to runoff is low and many of the rivers (termed 'dryland' rivers) cease to flow for extended periods of time, fragmenting into disconnected waterholes and wetlands (Davies *et al.* 1994; Tooth 2000; Bunn *et al.* 2006). The hydrologically variable dryland rivers of Australia are renowned for their periods of extensive flooding (the *boom*) and contrasting periods of extended drougt (the *bust*) (Walker *et al.* 1995; Bunn *et al.* 2006a). These contrasting states of flood and drought mean dryland rivers fluctuate between periods of high fragmentation (existing as numerous disconnected waterbodies) and periods of high connectivity across large areas of inundated floodplain (Sheldon *et al.* 2002). During dry periods, the disconnected waterholes represent the only permanent aquatic habitat in an otherwise dry landscape (Bunn *et al.* 2006a).

Previous studies of Australian dryland rivers have demonstrated the impact of variable hydrology on the spatial and temporal dynamics of a range of ecological patterns and processes, including benthic algae (McGregor *et al.* 2006), floodplain vegetation (Capon 2003), macroinvertebrates (Sheldon *et al.* 2002; Sheldon *et al.* 2003; Marshall *et al.* 2006), fish (Puckridge 1999; Puckridge *et al.* 2000; Arthington *et al.* 2005; Balcombe *et al.* 2007), waterbirds (Kingsford, 2010), benthic production (Burford *et al.* 2008; Fellows *et al.* 2009) and aquatic food webs (Bunn *et al.* 2003; Bunn *et al.* 2006b; Leigh *et al.* 2010). In many instances water quality, along with hydrology, has been seen as a key driver in explaining differences between no-flow and flow/flood phases (Puckridge 1999; Sheldon *et al.* 2002; Marshall *et al.* 2006; Leigh and Sheldon 2009). Using isotopic tracers, Hamilton *et al.* (2005) showed that during the no-flow phase, evaporative water loss dominates the hydrology and water chemistry in these isolated waterholes, and that spatial variation in water chemistry can be explained by differences in the level of flow required to trigger waterhole connection. Therefore, we may predict a greater variability in water quality and water chemistry in dryland rivers during the hydrological no-flow ('dry') phase, reflecting disconnection history.

The water quality and water chemistry of inland waterways reflects both external and internal processes. The surrounding geology (Stumm and Morgan 1996) and land-use (Ahearn *et al.* 2005) will influence the chemical constituents of the inflowing water during flow periods. During periods of no-flow, the interactions between evaporation, groundwater influence, concentration and precipitation of compounds and their adsorption onto particulate matter, and the resultant changes in ionic abundance will alter water quality at the local scale (Hamilton *et al.* 2005). There are very few studies focussing solely on the changes in water quality and water chemistry during hydrological cycles in large rivers, despite the recognition that water quality is a key driver in the compositional changes of many faunal groups (Close and Davies-Colley 1990; Sheldon *et al.* 2002; Arthington *et al.* 2005; Marshall *et al.* 2006) and functional processes (Biggs and Close 1989; Fellows *et al.* 2009).

Water quality is also a key component of water resource management, especially when water needs to comply with domestic drinking water guidelines (Hart *et al.* 1993, Hart *et al.* 1999). Increasingly, it is also a key component of assessments of river health (Hart *et al.* 1999; Yong and Chen 2002; Chang 2008; Bunn *et al.*, 2010). When using water quality data to assess ecosystem health, we need to be wary of the underlying natural variability within each river system and, specifically, variability associated with changing hydrology (see Sheldon 2005). To overcome the problem of specific water quality values being used to assess "health", both for drinking water and ecosystems, Hart *et al.* (1999) suggested the use of a 'risk-based' approach for establishing water quality guidelines, where trigger levels of risk are used based on an 'ecosystem-specific' understanding. Such an approach may be particularly useful for hydrologically variable rivers where variability in flow is likely to play a key role in water quality changes.

This study explored water quality changes in two Australian dryland rivers, Cooper Creek, Lake Eyre Basin, and the Warrego River, Murray-Darling Basin, across different hydrological phases from no-flow to flood over a number of years. We hypothesised that there would be maximum spatial variation in water quality and water chemistry during the no-flow phase when waterholes were disconnected and local processes were increasingly important. We also hypothesised that temporal changes in water quality across both rivers would reflect different phases of hydrology. Further, we use this information to reflect on ways in which appropriate water quality guidelines, so often used in river health assessment, could be established for dryland rivers.

Methods

Study area and sampling design

The dryland rivers studied were the lower reaches of Cooper Creek, a large inland river draining a large catchment (306,000 km^2), within the Lake Eyre Basin of Australia and the Warrego River, also a large lowland river, but draining a smaller catchment (78,400 km^2) within the upper Murray-Darling Basin, Australia (Fig. 1). Both rivers are characterised by low gradients, extensive floodplains and numerous waterholes. The region has highly variable annual rainfall, and both rivers have extremely variable flow, even in comparison to other dryland rivers (Puckridge *et al.* 1998; Young and Kingsford 2006) with long periods of no-flow typical (Fig. 2). Water quality of rivers and streams can reflect catchment geology and current land-use, and both Cooper Creek and the Warrego River could be regarded as near-pristine river systems. Upstream of the study region, Cooper Creek drains the north-eastern part of the Lake Eyre Basin. The geology of the region is dominated by clastic successions of Triassic and Jurassic age, part of the Great Artesian Basin (Galilee and Eromanga Basins, respectively) (GSQ 1975). The predominant land-use is low-level pasture grazing with limited cropping or irrigated agriculture. The Warrego River, in the upper Murray-Darling Basin drains a geology dominated by clastics of the Jurassic Surat basin (Evergreen sandstone and siltstone and Precipice sandstone) (GSQ 1975). The surrounding land-use is also low-level pasture grazing with limited cropping or irrigated agriculture. More details about the catchments can be found in McGregor *et al.* (2006), Bunn *et al.* (2006b) and Balcombe *et al.* (2007).

In each river, three or four waterholes were chosen from four reaches for a total of 15 waterholes per river (Fig. 1). The full set of waterholes in the Cooper Creek catchment were sampled on three occasions (April 2001, September 2001 and October 2002) covering two hydrological 'states'—no-flow (September 2001 and October 2002) and flow (April 2001) (Fig. 2; Table 1). To explore temporal patterns in Cooper Creek, a subset of four waterholes was sampled an additional four times (no-flow: October 2004 and December 2004 and flow: May 2003 and June 2003)), with two further sampling occasions during floodplain inundation or 'flood' (January and March 2004) (Fig. 2; Table 1). In the Warrego catchment the full set of waterholes were sampled on three occasions covering two hydrological 'states': no-flow (October 2001 and October 2002) and flow (April

2002), while the subset of four waterholes were sampled on the above three occasions and also in May 2003 (flow phase).

Sampling occasions were designated ‘no-flow’ if there was no indication of in-channel flow during the sampling trip and flow at the nearest gauge was 0 ML day^{-1}. For Cooper Creek, the nearest gauges were about 200 km upstream from the sampling locations, while for the Warrego Rivers the gauge was 100 km upstream, so in both situations conditions recorded at the site were used as the primary criteria for estimating flow. “Flow” was designated as in-channel flows, while “flood” refers to overbank flows.

Analysis

At each site on each sample occasion, a 10-L depth-integrated sample of the water column was collected and two sub-samples stored for water chemistry analysis in the laboratory. One sub-sample was kept at room temperature and analysed for electrical conductivity; the other sub-sample was frozen and analysed for total phosphorus (TP) and total nitrogen (TN). From the remaining water sample, conductivity, pH, turbidity, hardness, total dissolved solids (TDS) and total suspended solids (TSS) were quantified in the laboratory. Separate water samples collected at the same time were analysed for the major anions (Cl^-, HCO_3^-, and SO_4^{2-}) and cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) following standard methods (APHA 1998, EPA 1999). All samples were analysed to a NATA-accredited standard using methods detailed in Table 2.

Spatial and temporal patterns in water quality data were explored using Principal Components Analysis (PCA) in PRIMER v.5 (Clark and Gorley 2001). Analysis of similarities (ANOSIM) was used on the normalised Euclidean distance matrix to test for significant differences in overall water quality between the *a priori* defined groups of ‘waterholes’, ‘reaches’ and ‘flow phases’ (no-flow, flow and flood). Triangular coordinate plots (ternary diagrams) were used to compare the anion and cation concentrations at sites under different flow phases. Owing to both unequal variances between groups and unequal replication between the flow phases, Kruskal-Wallis and Mann-Whitney non-parametric tests were used to test for significant differences in median water quality parameters and anion and cation concentrations between the different flow phases in each river system.

Results

Water quality description

In Cooper Creek, water quality during the ‘no-flow’ phase was the most variable with coefficients of variation much higher than during the flood phase (Table 3). There were significant differences between the different flow phases for all parameters, apart from pH, TN and TP (Table 3). Conductivity, hardness and TDS were highest during the no-flow phase while turbidity was highest during the flood. In the Warrego River, water quality was also more variable across sites during the no-flow phase compared with the flow phase (Table 3), with significant differences in conductivity, turbidity, TSS, TN and TP. All parameters were highest during the no-flow phase compared with the flow phase.

Spatial and temporal patterns in water quality

The PCA of water quality data for the 15 sites on Cooper Creek over the two no-flow sample periods (September 2001 and October 2002) showed no distinct separation of water quality between waterholes with large variation (Fig. 3a); there were no consistent changes in water quality across the waterholes between the two sampling occasions. PC1 explained 49% of the variation and was associated with conductivity (PCA component loading of -0.483) and TDS (-0.493). PC2, explaining a further 30% of the variation, was associated with total hardness (-0.522), turbidity (-0.43) and total P (0.529). PC3 explained only 14% of the variation and was associated with TSS (0.493), total N (-0.549) and total P (-0.406). Two-way nested ANOSIM (waterholes nested within reaches) suggested no significant differences between the waterholes averaged across all reach groups (Global R = 0.081; p = 0.2), or between reaches using waterholes as samples (R = -0.067; p = 0.75). Although differences were not significant, the greatest variability in water quality (Fig. 3a) was in those waterholes in the Springfield reach, which were relatively dry across the two sampling periods, and two waterholes in the Tanbar reach (Yalungah and Yappi), which are relatively ephemeral and perhaps subject to the widest variations in hydrology.

Using the long-term data from the Windorah reach only, and classifying the trips by the predominant flow patterns at the time (no-flow, flow, flood), distinct patterns in water quality emerged (Fig. 3b). The first three principal components explained 96% of the variation in the dataset. PC1 explained 47% of the variation and related to conductivity (0.539), total hardness (0.531) and TDS (0.534). Trips were grouped along PC1 in accordance with the hydrology at the time of collection (Fig. 3b). PC2 explained a further

27% of the variation and was associated with the nutrients total N (0.666) and total P (0.703). PC3 explained a further 21% of the variation and was related to TSS (-0.766) and turbidity (-0.575). ANOSIM suggested significant differences in water quality between the three flow phases (Global R = 0.097, p = 0.033). Pair-wise comparisons suggested that the main difference was between the no-flow and flood phase.

As seen in Cooper Creek, PCA of water quality data for the 15 sites on the Warrego River over the two no-flow sample periods (October 2001 and October 2002) also showed no distinct separation of water quality between waterholes with large variation (Fig. 4a), or any consistent pattern of water quality change between the two sampling occasions. PC1 explained 61% of the variation and was associated with conductivity (-0.414), TDS (-0.413) and turbidity (-0.420). PC2 (18%), was associated with TSS (-0.621) and pH (0.449) while PC3 (15%) was associated with total hardness (-0.845). Two-way nested ANOSIM (waterholes nested within reaches) suggested significant differences between the waterholes averaged across all reach groups (R = 0.259; p = 0.025), and between reaches using waterholes as samples (R = 0.345; p = 0.01). Waterholes in the Quilberry and Thurulgoona reaches showed the greatest spatial variation.

Using the long-term data from the Binya reach only, and classifying the trips by the predominant flow patterns at the time (no-flow and flow), distinct patterns in water quality again emerged (Fig. 4b). The first three principal components explained 96% of the variation in the dataset. PC1 explained 75% of the variation and related to all variables with coefficients of approximately -0.3. Trips were grouped along PCI in accordance with the hydrology at the time of collection (Fig. 6b). PC2 (16%) was associated with turbidity (0.558) and total P (0.453) while PC3 (5%) was correlated with TSS (-0.592) and total N (0.521).

Patterns in ionic composition

The concentrations of the major anions and cations varied both spatially and temporally. In Cooper Creek, significant differences were found between the three flow phases for all major ions (Table 4) and Dunnett C post-hoc tests suggested all phases were significantly different from each other for all ions. Concentrations and variability, as the coefficient of variation, of all measured ions were greatest during the no-flow phase, suggesting considerable spatial variability between waterholes (Table 4; Fig 5a). The cationic dominance order for Cooper Creek was Na > Ca >> K > Mg while the anionic order was HCO_3 >> SO_4 > Cl.

In the Warrego River, significant differences were found between the two flow phases for concentrations of all the ions apart from bicarbonate, calcium and magnesium (Table 4). Again, concentrations and variability, as the coefficient of variation, differed between flow phases with the greatest variability during the no-flow phase, suggesting spatial variability between waterholes (Fig. 5b). The cationic dominance order for the Warrego River Creek was Na > Ca >> K > Mg while the anionic order was HCO_3 >> Cl > SO_4.

Ternary plots of anions and cations reinforce this ionic variability across the flow phases with the greatest dispersion within the no-flow phase for both Cooper Creek and the Warrego River (Figs. 5a and 5b). The ternary plots also reveal the similarity of the anion water chemistry of both Cooper Creek and the Warrego River with the world average freshwater values and vast difference to world average seawater (Fig. 5a and 5b). However, the opposite can be seen for cation chemistry, with both Cooper Creek and the Warrego River more similar to seawater than world average freshwater. The water chemistry is dominated by sodium, calcium and bicarbonate (Table 4).

Discussion

Spatial and temporal variability in water quality

In this study, we describe distinct differences in both the commonly measured water quality parameters across distinct hydrological phases (no-flow, flow and flood) in two dryland river catchments in Australia. The results supported both our hypotheses that spatial variation in water quality would be greatest during the no-flow phase when local processes were increasingly important and that temporal changes in water quality would reflect different phases of hydrology. Indeed, in both rivers, water quality was far more spatially variable during the no-flow period than during either the flow or flood phase, and, overall, the largest differences in water quality were driven by the temporal changes in flow. The spatial and temporal pattern of variability in water quality in these rivers mirrors the spatial and temporal variability observed in both diversity (Arthington *et al.* 2005; McGregor *et al.* 2006; Marshall *et al.* 2006) and processes (Fellows *et al.* 2009) within these river systems.

Spatial patterns in a range of water quality parameters have been reported for other river systems (eg. Cosumnes River, USA: Ahearn *et al.* 2004; Amu Darya River, Asia; Crosa *et al.* 2006; NSW Coastal Rivers, Australia: Markich and Brown, 1998; Shah *et al.* 2007; Han River, Korea: Chang 2008). Local spatial variation in parameters such as nutrients (Arhmeir and Lidén 2000), pH and salinity (Crosa *et al.* 2006) have been shown to be predominantly driven by catchment characteristics, such as local geology, landuse and forest cover. Larger spatial patterns in water quality are often driven by landscape scale processes, such as the underlying geology and evaporation conditions, such that the ionic composition of river water reflects the chemical interactions of the rock-water-atmosphere systems through which the river flows (Stumm and Morgan 1996; Wetzel 2001). In comparison, temporal variation in water quality datasets is usually described over longer timescales and attributed to anthropogenic land-use change (Yong and Chen 2002; Ahearn *et al.* 2005), or at shorter timescales and driven by seasonal flow (Arhmeir and Lidén 2000; Crosa *et al.* 2006).

Ionic composition

In many rivers of the world, it is the bicarbonate salts (calcium and magnesium) which dominate the chemical composition of river water, reflected in the position of “World Average Freshwater” (Cole 1983; Wetzel 2001) (Fig. 5). Within this average, however, the ionic composition of freshwater varies between continents and between regions within continents (Cole 1983). Wetzel (2001) provides a general comparison of the mean ionic concentrations of river waters of the world. His data for Australian rivers suggests a dominance of chloride but relatively equal concentrations of the cations Na^{+}, Mg^{2+}, and Ca^{2+}. Davies and Day (1998) described the geographical differences in ionic composition of lotic and lentic waterbodies in South Africa and distinguished between (i) rivers in which evaporation dominated and sodium and chloride formed the dominant ions, (ii) rivers draining igneous landscapes displaying a 'rock-dominated chemistry of calcium or magnesium bicarbonate, and (iii) rivers draining old weathered rocks, which again are dominated by sodium chloride.

In Cooper Creek and the Warrego River, there were no distinct spatial patterns in water quality that could be related to land-use or geology as there was little change either between sites or sampling times; rather, the major temporal changes reflected non-seasonal patterns of flooding and drying, while under no-flow conditions spatial differences seemed to reflect local-scale processes such as evaporation (Hamilton, *et al.* 2005). In both rivers, sodium, calcium and bicarbonate dominated the ionic composition of all samples, regardless of flow phase. This differs from Williams' (1983) description of the ionic composition of Australian inland lakes (isolated from river networks) in both the Lake Eyre and Murray-Darling Basins, where sodium chloride dominated. Much early work (Williams 1967; Williams *et al.* 1970; Williams and Buckney 1976) demonstrated the dominance of sodium and chloride in the ionic composition of lentic waterbodies across Australia. This Na-Cl dominance was attributed to the influence of marine sediments or 'cyclic accession of salt', where salt spray is transported inland from the sea in rain and dust such that the chemical composition of the inland water reflects marine origins (Williams 1983). Ephemeral saline lakes of the Paroo River catchment, Murray-Darling Basin were also found to be dominated by sodium chloride (Timms 1998). The relative anioic and cationic concentrations from both Cooper Creek and the Warrego River suggest dominance by sodium and calcium bicarbonate, which is consistent with what would be predicted in rivers draining catchments that are 'rock-dominated' (Davis and Day 1998), and consistent with the ionic chemistry from other lotic environments in Australia and elsewhere (Hart and McKelvie 1983; Davis and Day 1998; Markich and Brown 1998; Shah *et al.* 2007). Interestingly, Davies and Day (1998) suggested rivers with 'rock-dominated' ionic chemistry were draining catchments rich in igneous rocks, which is not the case for either Cooper Creek or the Warrego River. Rather, the dominance of bicarbonate in these rivers is perhaps suggestive of groundwater influence, where water in these large alluvial rivers is passing through carbonate-rich sediments and mixing with surface water.

Ecosystem health

Water quality is often a key parameter in measures of river and ecosystem health (Hart *et al.* 1999; Bunn *et al.* 2010). In hydrologically variable systems the problem with referential assessments of health stems from natural changes in indicators with increasing time since last flood (or connection) (Sheldon 2005). In the isolated waterholes of dryland rivers, increasing time since connection is often associated with a perceived 'deterioration' in some water quality parameters, such as increases in conductivity, TDS and nutrients. In Australia, water quality guidelines exist for a range of ecosystems and water uses (www.environment.gov.au/water/publications/quality/) (ANZECC 2000).For individual States, specific guidelines have been developed to allow the assessment of aquatic ecosystem health (or impact) based on compliance, with designated guideline values. In Queensland, water quality guidelines have been developed for the south-east coast, tropical coast and wet-dry tropics yet no information is presented for the inland rivers (DERM 2009). The dataset presented in this paper suggests that for highly variable inland rivers, water quality guidelines should be developed with respect to the 'flow phase'. During the no-flow phase, high levels of natural spatial variability may make the use of strict guidelines useless. This supports the work of Hart *et al.* (1999) who advocate "ecosystem-based" water quality guidelines, and the use of trigger values based on ranges, rather than strict values.

In summary, in the years since Jim Puckridge first began describing the variability of Australia's inland rivers, extreme spatial and temporal variability has been demonstrated in all aspects of their ecology (Sheldon *et al.* 2002; Arthington *et al.* 2005; Marshall *et al.* 2006; McGregor *et al.* 2006; Arthington *et al.* 2010; Kingsford *et al.* 2010), with water quality no exception. As one of the drivers of ecological pattern and process, establishing the variability in natural water quality across hydrological phases is an important step towards informing the future management of these unique rivers.

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Table 1. Average monthly flow for the month prior to water sample collection for both the Cooper Creek (Barcoo River, Retreat and Thompson River, Longreach Gauges) and Warrego River (Wyandra Gauge). Flow phase was determined based on criteria outlined in the text. For the Warrego River, April 2002, gauge readings at Wyandra were 0 ML day^{-1}, however, there was flow recorded at all sampling sites during sampling, therefore flow was estimated to be <1 ML day^{-1}.

	Average monthly flow (ML day^{-1})	**Flow phase**
Cooper sampling months		
April 2001	34.2	Flow
September 2001	0.0	No-flow
October 2002	0.0	No-flow
May 2003	21.5	Flow
January 2004	129,896	Flood
Feb/March 2004	27,205	Flood
June 2004	1.4	Flow
October 2004	0.0	No-flow
December 2004	0.0	No-flow
Warrego sampling months		
October 2001	0.0	No-flow
April 2002	<1.0	Flow
October 2002	0.0	No-flow
May 2003	11.3	Flow

Table 2. Summary of laboratory methods for determination of the different water quality parameters measured from collected water quality samples (APHA 1998). ICP refers to the inductively coupled plasma analysis method.

Parameter	**Analysis Method**	**Reference**
Turbidity	Nephelometric	APHA 2130B
Total Suspended Solids	Gravimetric	APHA 2540D
Total Dissolved Solids	Calculated	
Conductivity @ 25^{o}C	Conductivity cell	APHA 4500-H
pH	Electrometric	APHA 2510B
Sodium as Na^+	ICP	APHA 3120B
Potassium as K^+	ICP	APHA 3120B
Calcium as Ca^{2+}	Soluble ICP	APHA 3120B
Magnesium as Mg^{2+}	Soluble ICP	APHA 3120B
Chloride as Cl^-	IC/Titration	APHA 4110B
Sulphate as SO_4^{2-}	IC	APHA 4110B
Hardness as $CaCO_3$	Calculated	
Bicarbonate as HCO_3^-	Calculated	
Total Phosphorus (TP)	Automated Digestion	APHA 4500-P.F.
Total Nitrogen (TN)	Persulfate Digestion	APHA 4500-N.C.

Table 3. Summary statistics for water quality parameters and results of Kruskal-Wallis tests (χ^2) for differences between the three flow phases in Cooper Creek and Mann-Whitney U tests for differences between the two flow phases in the Warrego River.

			Conductivity uS cm^{-1} @ 25^oC	pH	Turbidity NTU	Hardness mg L^{-1}	TDS mg L^{-1}	TSS mg L^{-1}	Total N mg L^{-1}	Total P mg L^{-1}
Cooper Creek	Flood (n = 11)	Mean ± SE	95.1(5.3)	7.4 (0.05)	1036 (141)	23.1(2.03)	72.1 (3.2)	310.9 (43.7)	1.1 (0.06)	0.4 (0.04)
		Median	91.0	7.4	1000	22.0	69.0	350.0	1.1	0.4
		CV	0.19	0.02	0.45	0.29	0.15	0.47	0.19	0.33
	Flow (n = 23)	Mean ± SE	163.9 (11.9)	7.4 (0.04)	436 (80)	43.9 (3.6)	107.3 (6.7)	125.2 (54.1)	1.3 (0.18)	0.3 (0.03)
		Median	160.0	7.4	330	43.5	100.0	60.0	1.1	0.3
		CV	0.35	0.03	0.88	0.39	0.30	2.07	0.63	0.42
	No Flow (n = 39)	Mean ± SE	346.1 (39.2)	7.6 (0.04)	725 (152)	76.8 (5.8)	206.1 (23.2)	364.4 (82.9)	2.9 (0.49)	0.7 (0.09)
		Median	290.0	7.55	530	69.0	180.0	200.0	1.7	0.5
		CV	0.71	0.03	1.31	0.47	0.70	1.42	1.05	0.85
	Kruskal-Wallis test (χ^2)		17.81, $p<0.001$	0.196, $p>0.05$	14.68 $p<0.001$	17.02 $p<0.001$	14.03 $p<0.001$	11.46 $p=0.001$	0.248 $p>0.05$	χ^2 =2.34 $p>0.05$
Warrego River	Flow (n = 19)	Mean ± SE	151.0 (20.6)	7.29 (0.07)	494 (96)	36.9 (2.6)	93.8 (12.2)	59.5(5.8)	1.0 (0.10)	0.3 (0.06)
		Median	110.00	7.25	380	34.5	71.0	60.0	0.8	0.2
		CV	0.60	0.04	0.85	0.31	0.57	0.42	0.46	0.82
	No Flow (n = 31)	Mean ± SE	252.4 (44.3)	7.42 (0.07)	755 (87)	42.9 (2.8)	151.3 (26.2)	180.6 (26.4)	1.5 (0.18)	0.7 (0.16)
		Median	150.00	7.35	550	41.5	87.0	130.0	1.1	0.4
		CV	0.98	0.05	0.65	0.36	0.96	0.81	0.67	1.25
	Mann-Whitney U		188.5 $p<0.05$	227 $p>0.05$	156.5 $p<0.01$	213.5 $p>0.05$	202.5 $p >0.05$	86.5 $p<0.001$	139 $p<0.01$	U = 107 $p<0.001$

Table 4. Summary statistics for anions and cations (mg L^{-1}) and results of Kruskal-Wallis tests for differences between the three flow phases in Cooper Creek and Mann-Whitney U tests for differences between the two flow phases in the Warrego River.

		Cooper Creek				**Warrego River**		
		No-Flow	**Flow**	**Flood**	**Kruskal-Wallis Test (χ^2)**	**No-Flow**	**Flow**	**Mann-Whitney U**
Sodium (Na^+)	Mean (± *SE*)	39.7 *(7.2)*	14.8*(1.2)*	7.5 *(0.4)*	43.0, $p<0.001$	35.9 *(10.4)*	15.9 *(4.9)*	172, $p<0.05$
	Median	26.5	13.5	7.9		10.0	7.5	
	CV	1.69	0.42	0.15		1.62	1.34	
Potassium (K^+)	Mean (± *SE*)	8.0 *(0.7)*	4.7 *(0.4)*	4.0 *(0.3)*	25.6; $p<0.001$	5.1 *(0.2)*	4.0 *(0.8)*	136, $p<0.01$
	Median	6.9	4.2	4.5		4.7	3.6	
	CV	0.61	0.44	0.23		0.27	0.19	
Calcium (Ca^{2+})	Mean (± *SE*)	20.9 *(1.5)*	12.0 *(1.0)*	6.4 *(0.7)*	35.1, $p<0.001$	11.3 *(0.8)*	9.5 *(0.7)*	208, $p>0.05$
	Median	19.0	12.0	5.9		11.0	8.8	
	CV	0.51	0.38	0.38		0.38	0.32	
Magnesium (Mg^{2+})	Mean (± *SE*)	6.0 *(0.5)*	3.4 *(0.3)*	1.7 *(0.1)*	37.2; $p<0.001$	3.6 *(0.2)*	3.2 *(0.2)*	236, $p>0.05$
	Median	5.3	3.3	1.7		3.6	3.1	
	CV	0.62	0.41	0.23		0.34	0.29	
Chloride (Cl^-)	Mean (± *SE*)	20.3 *(4.0)*	8.3 *(0.6)*	2.4 *(0.1)*	36.9; $p<0.001$	17.8 *(4.8)*	8.8 *(2.3)*	173, $p<0.05$
	Median	13.0	8.3	2.0		7.2	3.6	
	CV	1.9	0.38	0.25		1.51	1.16	
Bicarbonate (HCO_3^-)	Mean (± *SE*)	137.3 *(13.8)*	72.9 *(7.3)*	46.3 *(2.7)*	32.5; $p<0.001$	115.1 *(19.9)*	68.8 *(9.5)*	199, $p>0.05$
	Median	125.0	70.0	43.5		65.0	49.0	
	CV	0.68	0.49	0.21		0.96	0.6	
Sulphate (SO_4^{2-})	Mean (± *SE*)	25.3 *(4.5)*	9.2 *(0.8)*	6.2 *(0.5)*	28.6; $p<0.001$	6.1 *(0.5)*	4.4 *(0.4)*	153, $p<0.01$
	Median	19.0	9.8	5.6		5.1	4.0	
	CV	1.48	0.37	0.32		0.5	0.37	

Figure Legends

Fig. 1. Locations of waterholes sampled in the Cooper Creek and Warrego River catchments. Individual waterholes are indicated with circles. From Fellows et al. (2009).

Fig. 2. Hydrographs for the sampling period for (a) Cooper Creek and (b) Warrego River. Cooper Creek discharge is the sum of the discharges recorded from gauges on the Barcoo River at Retreat and Thompson River at Stonehenge. Warrego River discharge is from the Wyandra gauge on the Warrego River. Sampling dates are represented with arrows. Hydrology data were obtained from the Queensland Department of Natural Resources and Mines (2005).

Fig. 3 Principal Components Analysis (PCA) of water quality parameters collected from sites in Cooper Creek between 2001 and 2004 (a) 15 sites sampled during a no-flow phase in September 2001(open symbols) and October 2002 (closed symbols) and (b) centroids (± x,y SE) of PCA of Windorah samples only from April 2001 to December 2004 grouped by flow phase.

Fig. 4. Principal Components Analysis (PCA) of water quality parameters collected from sites in the Warrego River between 2001 and 2003 (a) 15 sites sampled during the no-flow phases of October 2001 (open symbols) and October 2002 (closed symbols) and (b) centroids (± x,y SE) of PCA of Binya samples only from October 2001 to May 2003 grouped by flow phase

Fig. 5. Ternary diagrams showing the major ionic composition, percentages are based on mol L^{-1}, for (a) Cooper Creek and (b)Warrego River for all samples collected across all flow phases. Averages for world freshwater (open triangle) and Australian freshwater (open square) from Wetzel (2001). World average seawater (open circle) from Cole (1983).

Figure 1

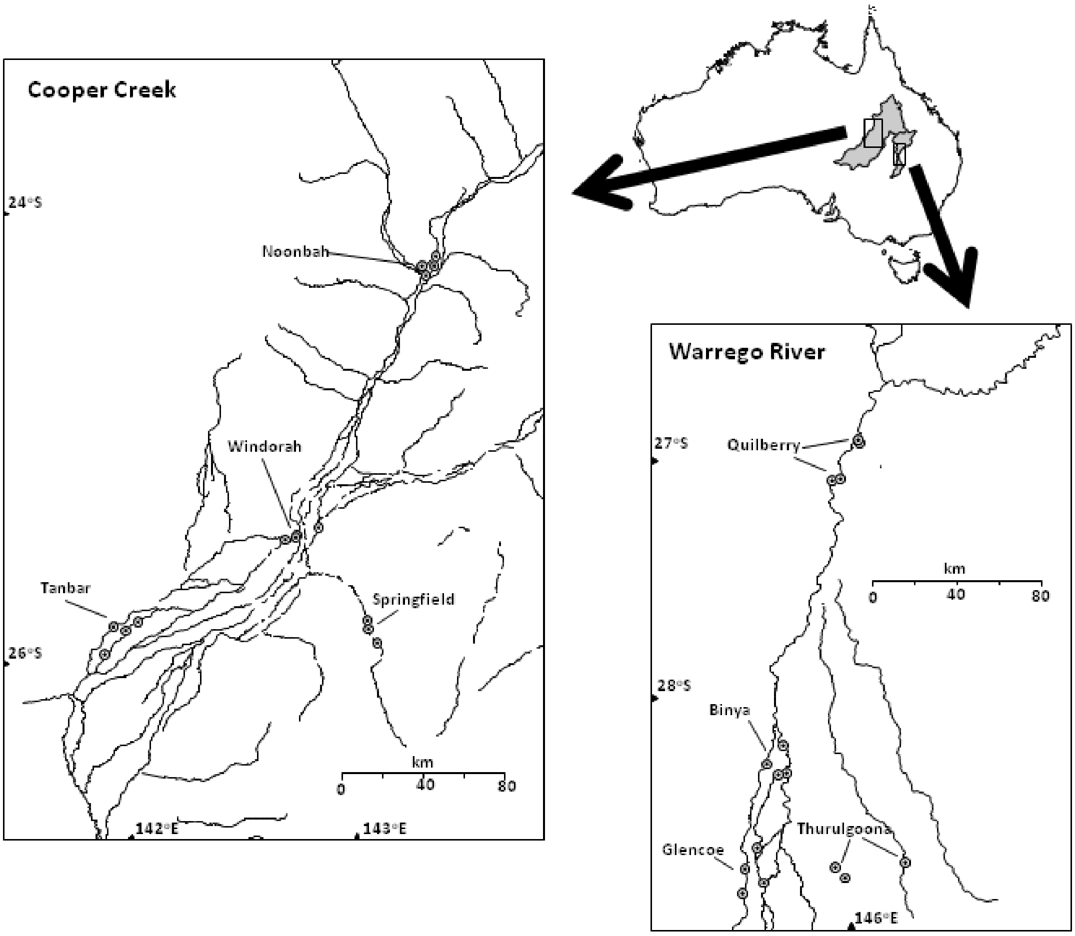

Cooper Creek
24°S
Noonbah
Windorah
Tanbar
Springfield
26°S
km
0
40
80
142°E
143°E
Warrego River
27°S
Quilberry
km
0
40
80
28°S
Binya
Glencoe
Thurulgoona
146°E

Figure 2

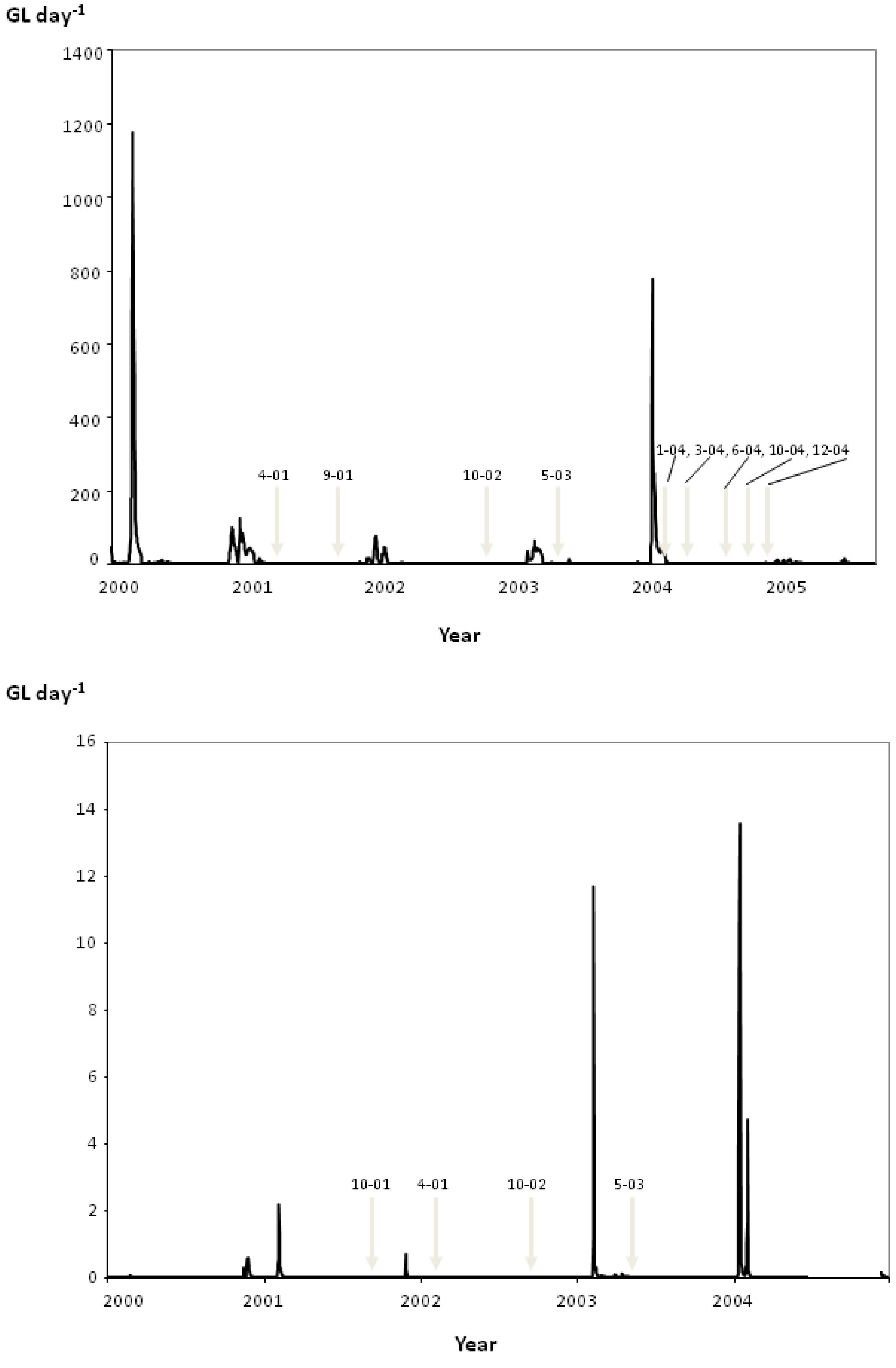

GL day-1
1400
1200
1000
800
600
400
200
0
2000
2001
2002
2003
2004
2005
Year
4-01
9-01
10-02
5-03
1-04, 3-04, 6-04, 10-04, 12-04
GL day-1
16
14
12
10
8
6
4
2
0
2000
2001
2002
2003
2004
Year
10-01
4-01
10-02
5-03

Figure 3

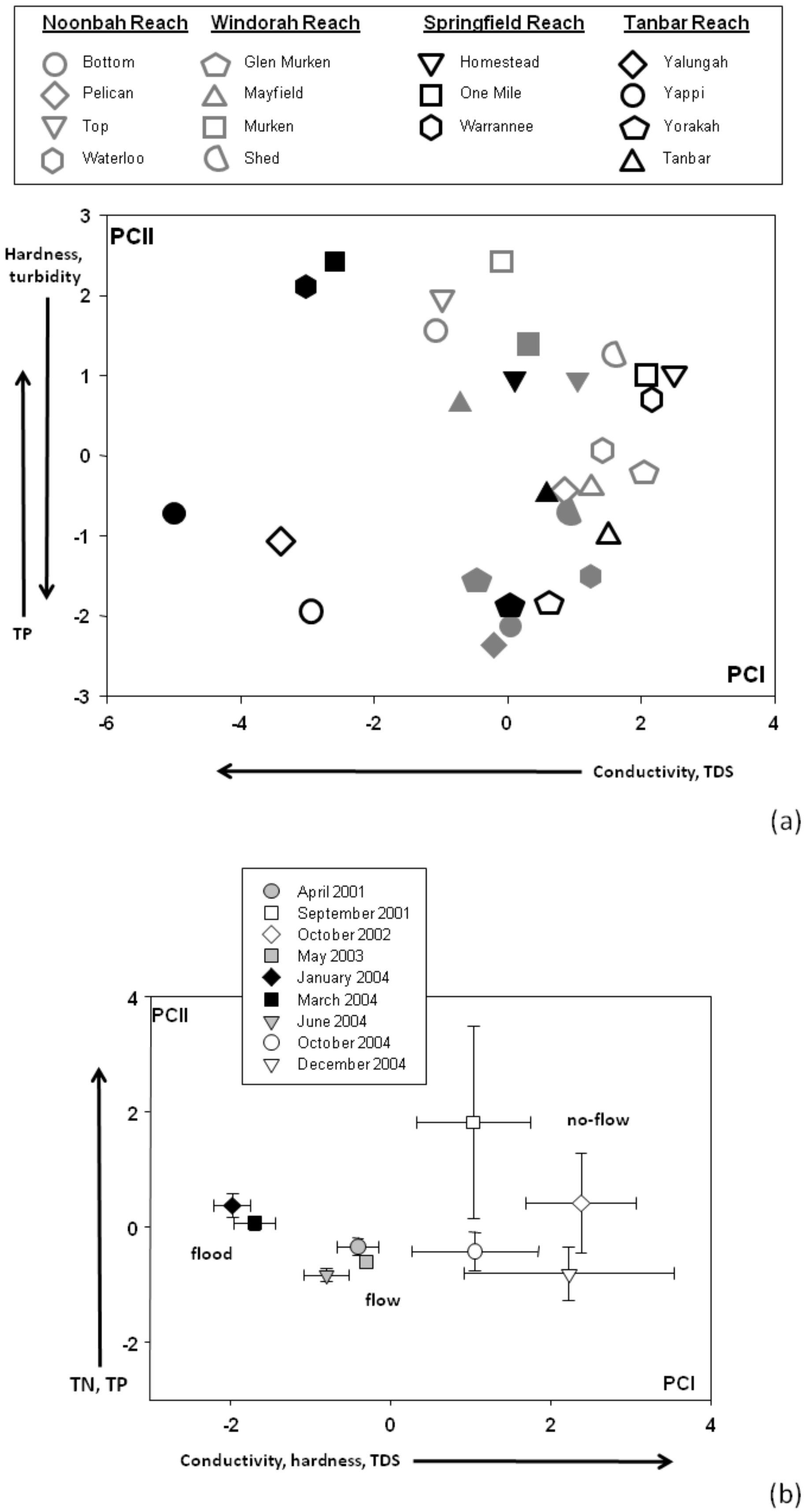

Noonbah Reach
Bottom
Pelican
Top
Waterloo
Windorah Reach
Glen Murken
Mayfield
Murken
Shed
Springfield Reach
Homestead
One Mile
Warrannee
Tanbar Reach
Yalungah
Yappi
Yorakah
Tanbar
PCII
PCI
Hardness, turbidity
TP
Conductivity, TDS
3
2
1
0
-1
-2
-3
-6
-4
-2
0
2
4
(a)
April 2001
September 2001
October 2002
May 2003
January 2004
March 2004
June 2004
October 2004
December 2004
PCII
PCI
4
2
0
-2
-2
0
2
4
no-flow
flood
flow
TN, TP
Conductivity, hardness, TDS
(b)

Figure 4

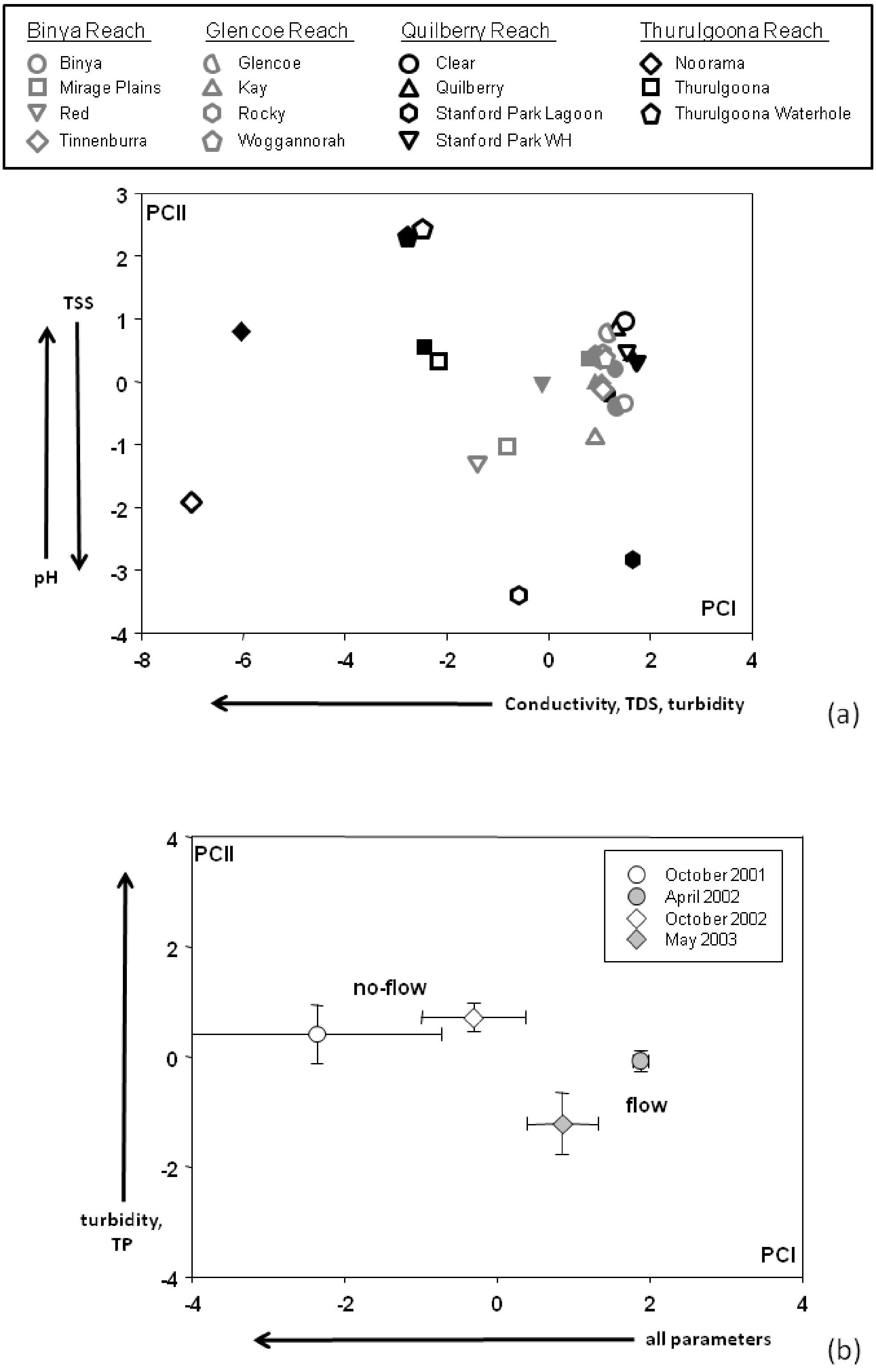
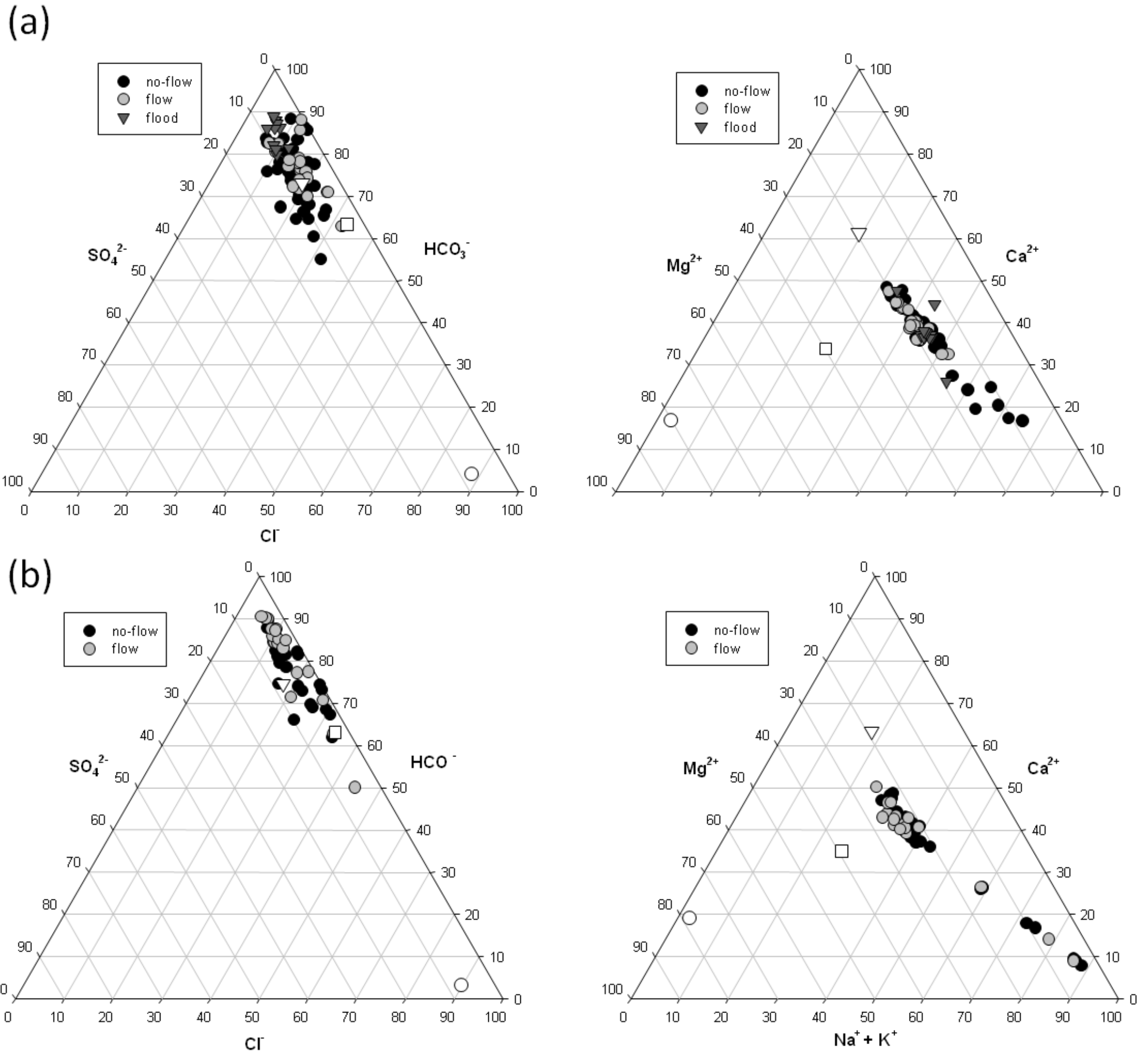

Binya Reach
Binya
Mirage Plains
Red
Tinnenburra
Glencoe Reach
Glencoe
Kay
Rocky
Woggannorah
Quilberry Reach
Clear
Quilberry
Stanford Park Lagoon
Stanford Park WH
Thurulgoona Reach
Noorama
Thurulgoona
Thurulgoona Waterhole
PCII
PCI
TSS
pH
Conductivity, TDS, turbidity
3
2
1
0
-1
-2
-3
-4
-8
-6
-4
-2
0
2
4
(a)
PCII
PCI
October 2001
April 2002
October 2002
May 2003
no-flow
flow
turbidity, TP
all parameters
4
2
0
-2
-4
-4
-2
0
2
4
(b)

Figure 5


(a)
no-flow
flow
flood
SO_4^{2-}
HCO_3^-
Cl^-
Mg^{2+}
Ca^{2+}
0
10
20
30
40
50
60
70
80
90
100
(b)
no-flow
flow
SO_4^{2-}
HCO^-
Cl^-
Mg^{2+}
Ca^{2+}
$Na^+ + K^+$