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Hydrochemical assessment of the Hutton and Precipice sandstones in the northern Surat Basin

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Executive summary

This report forms a component of the GISERA project 'Constraining groundwater flow rates in the Surat Basin through environmental tracer and hydrochemical data'. Although the conceptual understanding of groundwater flow processes in the Surat Basin, Queensland, has improved substantially over the last few years, there continue to be critical knowledge gaps that need to be addressed to be confident that impacts on the groundwater balance from coal seam gas (CSG) extraction are negligible. Especially in the northern part of the Surat Basin, there is an on-going discussion about recharge processes and rates as well as groundwater flow directions within key agricultural aquifers such as the Hutton Sandstone and the Precipice Sandstone and whether these could be affected by CSG extraction.

In this component of the GISERA project, hydrochemical data were compiled and then used to assess regional scale recharge processes, hydrochemical evolution along groundwater flow paths and the influence of faulting on groundwater flow and hydrochemistry. Following extensive data quality control checks, a multi-variate statistical analysis was conducted. This statistical assessment was complemented by comparing the ratios of major ions relative to chloride. This approach allowed the identification of major hydrochemical processes affecting the hydrochemical evolution of groundwater along deep regional scale flow paths.

For the Precipice Sandstone, the assessment demonstrated that there is some hydrochemical variability, although the overall differences between hydrochemical clusters are relatively minor. This is likely due to a relatively homogeneous lithological composition of this aquifer. Hydrochemistry also confirmed that one of the major regional faults in the Surat Basin, the Burunga Leichhardt fault, may form a pathway that connects the Precipice Sandstone to the more shallow overlying aquifers.

Compared to the Precipice Sandstone, the Hutton Sandstone displayed a much higher hydrochemical variability, with salinities ranging from very fresh to saline, and a wide range of ion ratios. The spatial assessment of the hydrochemical clusters showed that a northerly flow component within the Hutton Sandstone is possible, as previously suggested by other studies based on potentiometric surfaces. Furthermore, the assessment also showed that localized recharge occurs within the western outcrop areas of the Hutton Sandstone, where groundwater is very fresh (electrical conductivity less than approximately 500 µS/cm) and shows hydrochemical attributes associated with recharge waters.

Overall, the study demonstrated the value of baseline hydrochemistry data to test existing hydrogeological conceptualizations and where robust evidence is available to improve such conceptualizations to better inform the potential impacts from CSG depressurization on adjacent aquifers. The study identified key knowledge gaps, including geographic areas where additional hydrochemical data collection could help to improve the understanding of hydrodynamics in the northern Surat Basin.

The hydrochemical assessment presented in this report will inform other tasks within this GISERA project, and form the basis for further testing of the conceptual hydrogeological understanding of these key aquifers in the northern Surat Basin.

1 Introduction

Conceptual understanding of groundwater recharge mechanisms, recharge rates and flow directions in the northern Surat Basin has evolved over the last two decades as more groundwater and stratigraphic data became available from groundwater resource investigations and coal seam gas exploration and associated groundwater monitoring programmes (e.g. Office of Groundwater Impact Assessment, 2016). However, there is a recognition that additional work is required to close some of the remaining knowledge gaps. A particular area within the northern part of the Surat Basin where knowledge gaps were identified is the Dawson River catchment, which partly overlies a major geological structural feature known as the Mimosa Syncline (Figure 1). Key aquifers of the Surat Basin such as the Hutton Sandstone and the Precipice Sandstone sustain agricultural developments and town water supplies in the northern Surat Basin (e.g. Welsh et al., 2014; Office of Groundwater Impact Assessment, 2016). They outcrop in the northern part of this area and dip towards the south, where they are confined underneath younger stratigraphic formations (Figure 1).

The Early Jurassic Precipice Sandstone is the oldest unit of the Surat Basin. It comprises thick-bedded, coarse, quartzose sandstone (Whitehouse, 1952; 1955), and it is conformably overlain by the Evergreen Formation. It is absent in some areas where the Evergreen Formation unconformably sits on pre-Jurassic units (Cook et al., 2013).

The Hutton Sandstone overlies the Evergreen Formation and underlies the Walloon Coal Measures. It comprises quartzose to sublabile sandstones with rare interbedded siltstone and coarser beds (Cook et al., 2013), and was deposited in a braided fluvial system where sandstone units represent stacked channel sands (e.g. Moore et al., 1986; John and Almond, 1987; Gray et al., 2002). Green (1997) divided the Hutton Sandstone into 'upper' and 'lower' members based on the 'lower' containing relatively more siltstone.

Within the Dawson River catchment in the northern Surat Basin, an area where significant coal seam gas exploration and development has occurred during the last years, there is uncertainty surrounding groundwater flow directions in parts of the Hutton Sandstone and within the Precipice Sandstone. Understanding of groundwater flow directions is important because it provides indication of the nature of interactions between surface water and groundwater, between shallow and deep aquifers, and it is part of the evidence base to interpret the role of geological faults on regional groundwater flow. Based on drill stem test pressure data of petroleum wells and water level measurements from groundwater bores, Hodgkinson and Grigorescu (2012) indicated that there is potential for a significant northerly flow component from Chinchilla and from the south-west (Injune, Figure 1) towards Taroom (Figure 2). Hodgkinson et al. (2010) found similar results for the Evergreen Formation and Precipice Sandstone. Similar to the northwards groundwater flow direction proposed by Hodkinson and Grigorescu (2012), Ransley and Smerdon (2012) and Ransley et al. (2015) suggested that there is groundwater loss to river baseflow from GAB aquifer outcrop areas where the Dawson River is deeply incised into the Hutton and Precipice sandstones (Figure 3). They estimated approximately 8623 ML/year of groundwater flow loss from the GAB intake beds (mainly Hutton Sandstone) to the Dawson River, and suggested that this could account for some of the northward flow directions proposed by Hodgkinson and Grigorescu (2012). Similar patterns were also suggested by the Office of Groundwater Impact Assessment (Office of Groundwater Impact Assessment, 2016); this work indicated that there is topographically driven groundwater flow towards the north and north-east in the Hutton and Precipice sandstones north of the Great Dividing Range, and that recharge around the northern margin may not contribute significantly to the deeper parts of the Great Artesian Basin. This was further indicated by Underschultz and Vink (2015) for the Hutton Sandstone based on potentiometric surfaces and a multivariate statistical assessment of groundwater chemistry.

The finding of a northerly groundwater flow is somewhat counter-intuitive, as groundwater recharge in sedimentary bedrock aquifer systems is generally expected to result from infiltrating rainwater within the outcrop areas, and groundwater flow is then expected to follow the sedimentary bedrock topographic gradient away from the intake beds and towards the deeper parts of the sedimentary basin (in case of the northern Surat Basin toward the south-west) (Figure 4). Because of the potential existence of a northerly flow path towards the recharge area and against the bedrock topographic gradient, a perceived paradox exists.

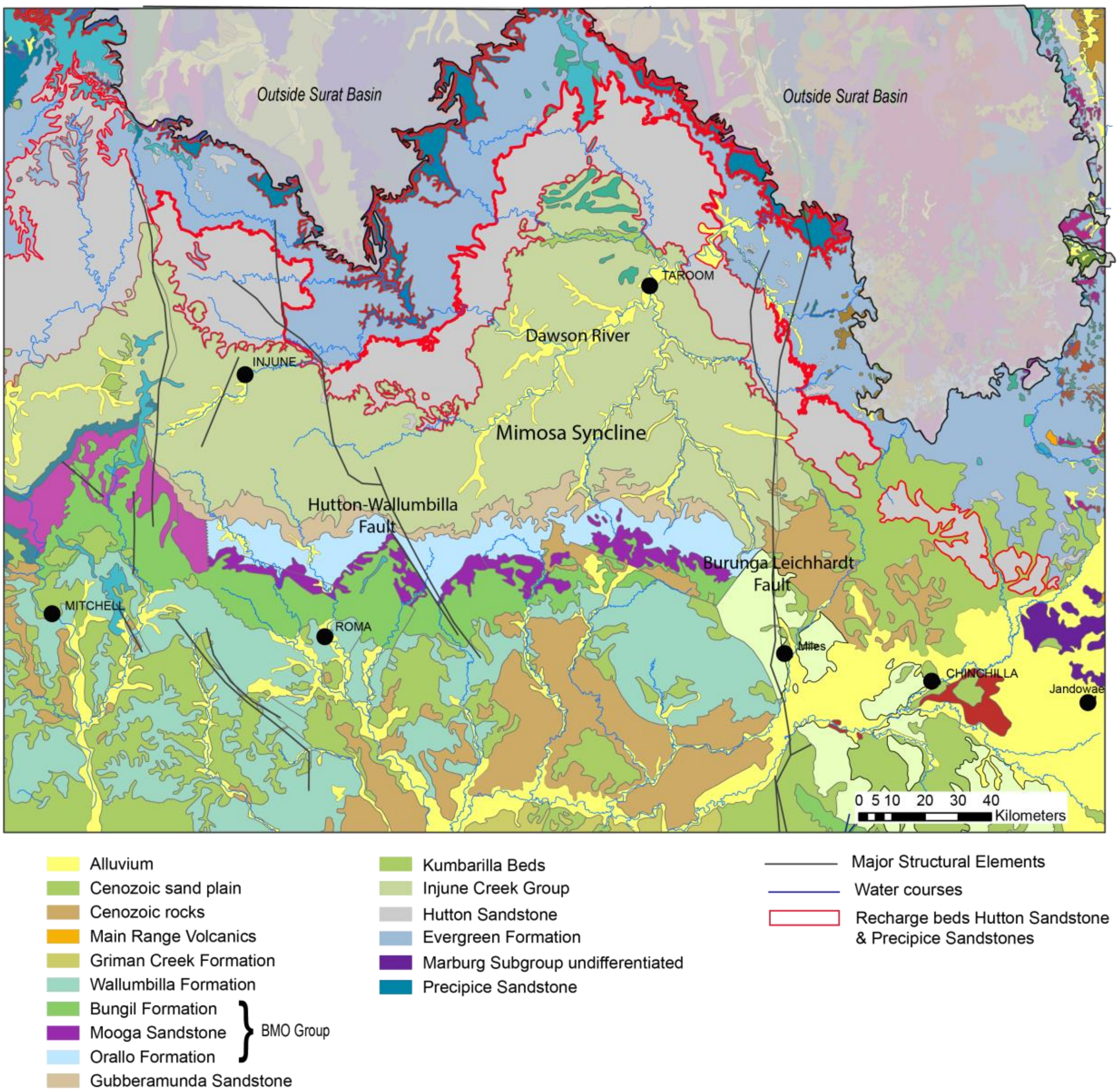

Figure 1 Geological map of the northern Surat Basin

Previous isotope tracer work by Suckow et al. (2016) aimed to assess this perceived paradox for the Hutton Sandstone. The isotope work conducted by Suckow et al. (2016) indicated that there is a tendency for groundwater ^{14}C and ^{36}Cl tracer concentrations to decrease from north to south in the Mimosa Syncline (Figure 1), suggesting that the main direction for groundwater flow is from north to south. However, the authors also suggested that even though the observed tracer patterns are consistent with a general north-southerly flow direction, more diverse local-scale flow directions are possible within the Hutton Sandstone. Suckow et al. (2016) also suggested that the Hutton Sandstone forms a double-porosity system, where groundwater flow is largely restricted to the more transmissive channel deposits. Following the work by Suckow et al. (2016), it was evident that additional environmental tracer samples are required to improve the understanding on groundwater flow dynamics in the Hutton Sandstone. Furthermore, as only few environmental tracer measurements existed within the Precipice Sandstone, it became evident that there is limited understanding on flow rates and groundwater flow directions within this important agricultural aquifer. The recognized data and knowledge gaps led to the development of the present project 'Constraining groundwater flow rates in the Surat Basin through environmental tracer and hydrochemical data' – GISERA W6 (https://gisera.org.au/project/improving-groundwater-flow-models/).

1.1 Aims of this report

This report forms Task 3 within the GISERA W6 project 'Constraining groundwater flow rates in the Surat Basin through environmental tracer and hydrochemical data'. The aims of this component and the associated report are to:

- Compile hydrochemical data particularly for the Hutton Sandstone and Precipice Sandstone from groundwater databases (DNRM, 2016), previous reports (e.g. Feitz et al., 2014; Ransley et al., 2015; Suckow et al., 2016) and coal seam gas companies' monitoring programmes;
- Use 3D geological models provided by the Qld Office of Groundwater Impact Assessment (OGIA) (Office of Groundwater Impact Assessment, 2016) together with other geological data and a 3D geological model developed by CSIRO (Raiber, unpublished) to refine the aquifer assignment of groundwater bores and increase confidence in bore-aquifer assignments;
- Assess the spatial variability of hydrochemistry within the Hutton Sandstone and Precipice Sandstone in the northern Surat Basin, using multivariate statistical analyses (hierarchical cluster analysis, HCA) and graphical techniques (e.g. ion ratio plots); determine if the observed patterns provide new insights into groundwater flow paths in the northern Surat Basin;
- Determine if there are any within-aquifer hydrochemical differences that can be linked to hydrological processes such as aquifer interactions or the influence of faults; this will be used to test the current conceptual understanding of hydrogeological processes, particularly in the Dawson River area;
- Inform the environmental tracer sampling campaign (Component 2 of GISERA W6, completed in March/April 2017);
- Inform numerical groundwater and reactive transport model development (Component 4 of GISERA W6);

- Identify key knowledge gaps that can inform future data collection and sampling campaigns.

In this task of the GISERA W6, hydrochemical data are used as an independent line of evidence to test the current conceptual understanding of regional groundwater flow and recharge patterns in the Hutton Sandstone and Precipice Sandstone in the northern Surat Basin. The key for this project is the reliable knowledge of the source aquifer from which the sample was collected. Only with this knowledge hydrochemical data can be used to assess intra and inter-aquifer flow patterns and hydrochemical processes from the recharge area to the deeper parts of the Surat Basin. The aquifer membership of bores in the current version of the QLD groundwater database (DNRM, 2016) is sometimes incorrect, ambiguous or unknown, and the screened intervals of bores sometimes source water from different aquifers than stated in the database. Therefore, perceived within-aquifer changes of hydrochemistry might indeed represent differences between different aquifers, potentially leading to misinterpretations. To avoid such issues and resulting misconceptions, an existing 3D geological model of the aquifer boundaries (formation tops) developed and provided by the Queensland Office of Groundwater Impact Assessment (Office of Groundwater Impact Assessment, 2016) was used to verify that only water chemistry records are included in the assessment of spatial patterns where the aquifer membership can be determined with a high level of confidence. For the identification of hydrochemical changes along inferred flow-paths based on hydraulic heads, multivariate statistical techniques were applied and major ion ratios were assessed. This aimed to identify hydrochemical characteristic fingerprints within the Hutton Sandstone and Precipice Sandstone aquifers along inferred flow paths and to understand the controlling factors (e.g. hydrochemical processes or inter-aquifer mixing) of spatial variability. However, it is important to note that these groundwater head measurements used to derive flow paths represent post-agricultural development flow conditions. Furthermore, hydraulic pressures in sedimentary bedrock aquifers are likely to respond substantially faster to anthropogenic stresses than hydrochemistry or tracers, which particularly in deeper parts of sedimentary bedrock aquifers are expected to take hundreds or thousands of years before the hydraulic changes significantly influence the hydrochemical or isotopic signature (Zuber et al. 2011).

Task 3 is linked closely and iteratively with Task 2 (‘Collection and analysis of age tracer data’) of this project. For example, the initial hydrochemical assessment conducted as part of Task 3 helped to decide on the optimal environmental tracer sampling locations, and the hydrochemical data collected as part of the environmental tracer sampling campaign fed back into the assessment of hydrochemical processes in the northern Surat Basin. The refined conceptual models and quality-checked hydrochemical data then inform Task 4 (‘Integrated age tracer/reactive transport model’).

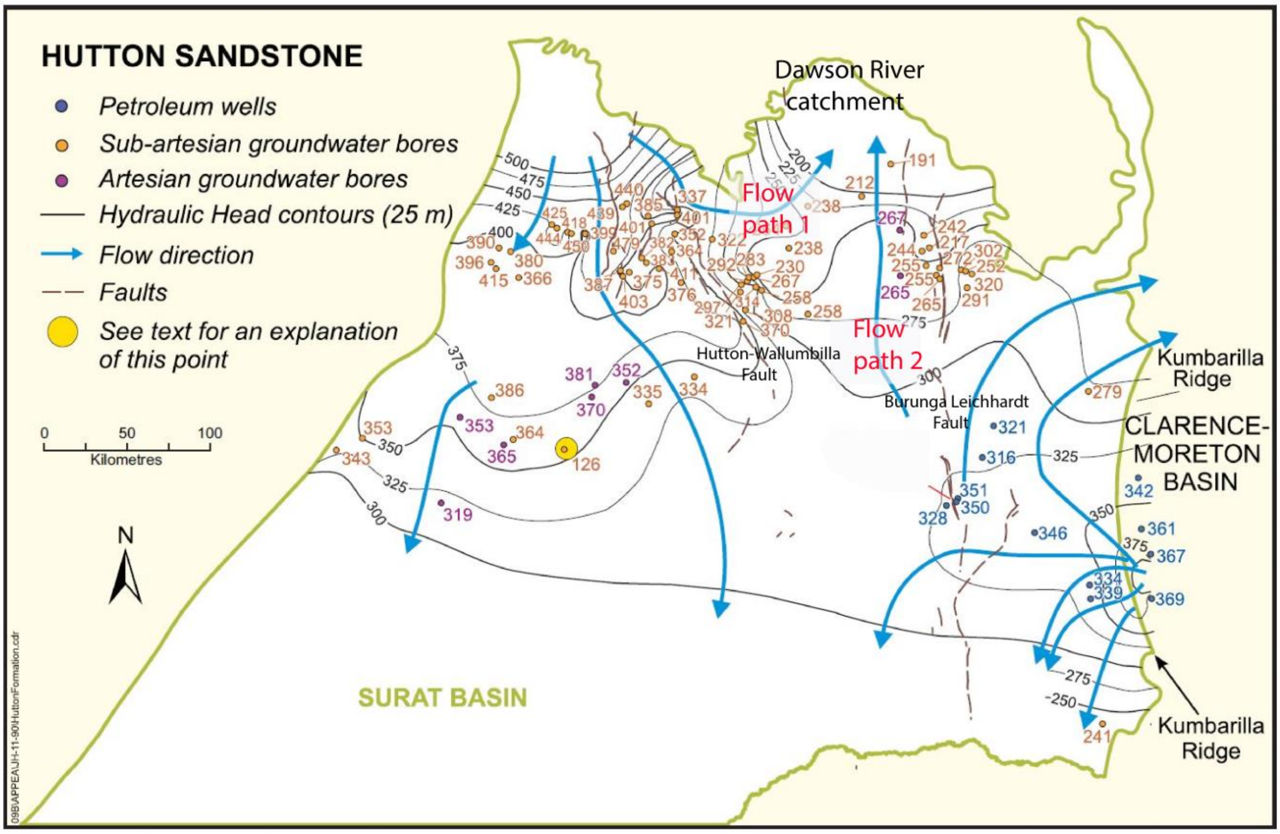

Figure 2 Potentiometric surface for the Hutton Sandstone inferred by geophysical methods (modified from Hodgkinson et al. 2010). The two hypothesized flow paths marked as 'Flow path 1' and 'Flow path 2' in the Dawson River catchment will be assessed further using hydrochemistry in this report.

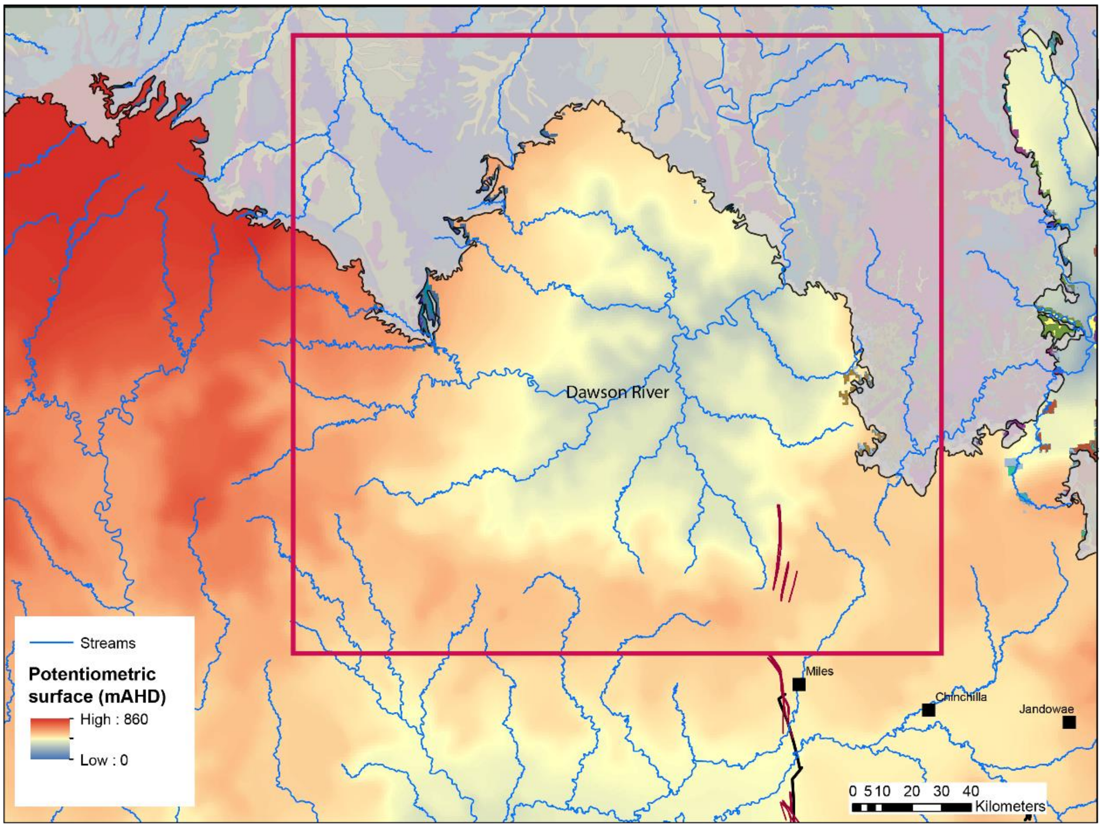

Figure 3 Potentiometric surface for the Hutton Sandstone in the vicinity of the Dawson River catchment (Ransley and Smerdon, 2012)

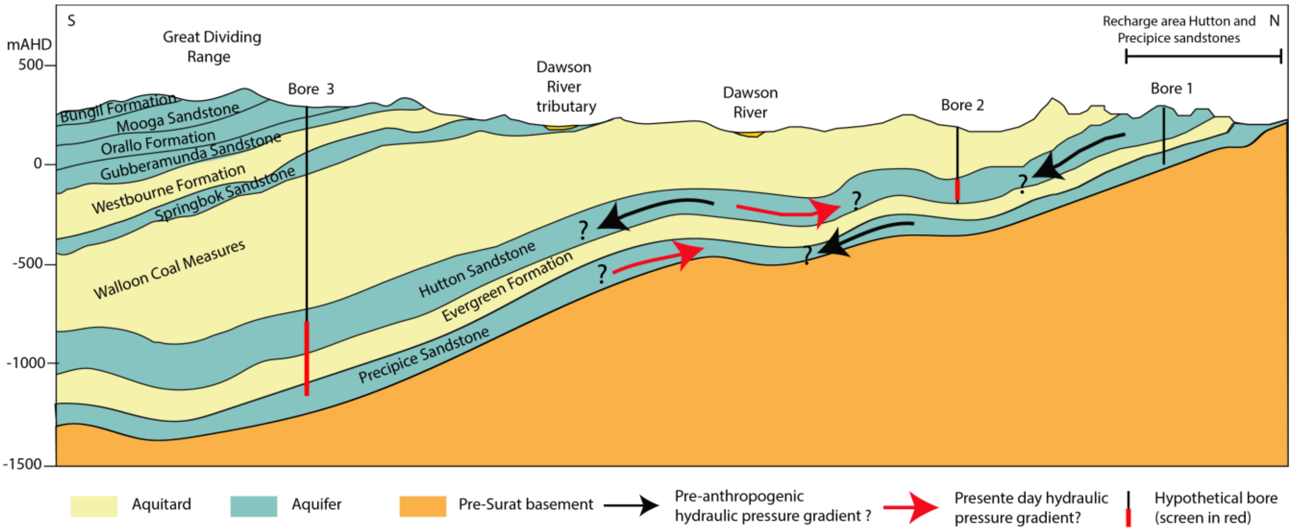

Figure 4 Cross-section through the northern Surat Basin (Mimosa Syncline) modified from Mallants et al. (2017); black and red arrows mark potential southwards pre-anthropogenic (inferred from the bedrock gradient) and present day northwards hydraulic pressure gradients (suggested for example by Hodgkinson and Grigorescu (2013), GABWRA (Ransley and Smerdon, 2012), and Underschultz and Vink (2015)), to be tested using hydrochemical data in this report. The classification as 'aquifer' or 'aquitard' is a generalisation only, as there are considerable within-formation differences.

2 Methodology

2.1 Aquifer assignments

Lithological and stratigraphic data, bore construction details and historical water level and water chemistry records were compiled from the Queensland Department of Natural Resources and Mines (DNRM) groundwater database (DNRM, 2016). Figure 5 highlights that there are a considerable number of groundwater bores (~3800) in the Dawson River area within the northern Surat Basin. However, as also shown on Figure 5, there are only a relatively small number of bores in the outcrop areas of the Hutton Sandstone and Precipice Sandstone at the western margin of the Mimosa Syncline.

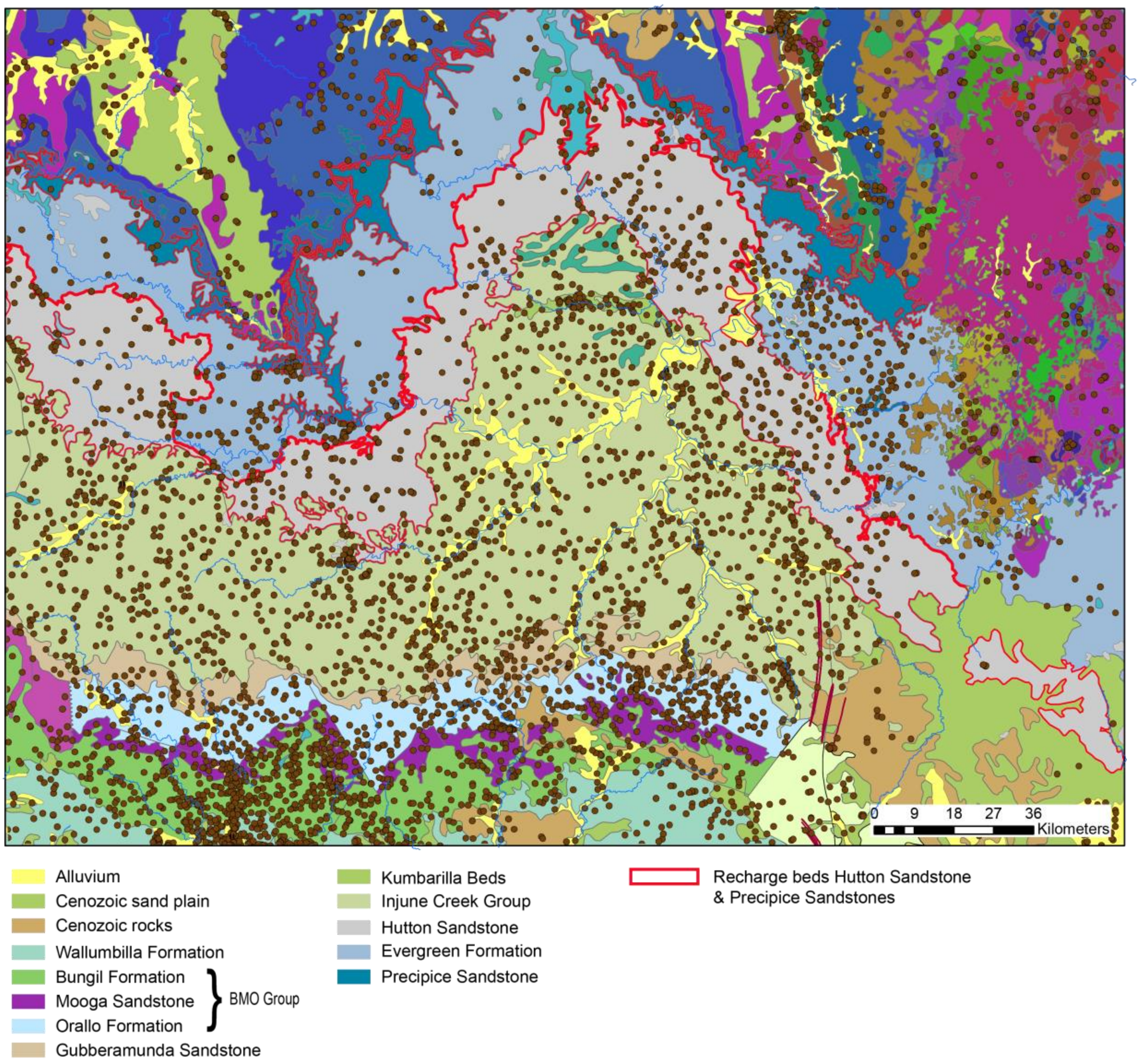

Figure 5 Groundwater bore locations in Queensland groundwater database in the northern Surat Basin (DNRM, 2016)

Groundwater chemistry data were also sourced from coal seam gas companies.

Figure 6 shows all bores with hydrochemical data in the Queensland groundwater database (DNRM, 2016). The comparison with Figure 5 highlights that less than 20% of all bores within this area have any hydrochemical records, and only few hydrochemical records exist for bores in the outcrop areas of the Hutton Sandstone and Precipice Sandstone.

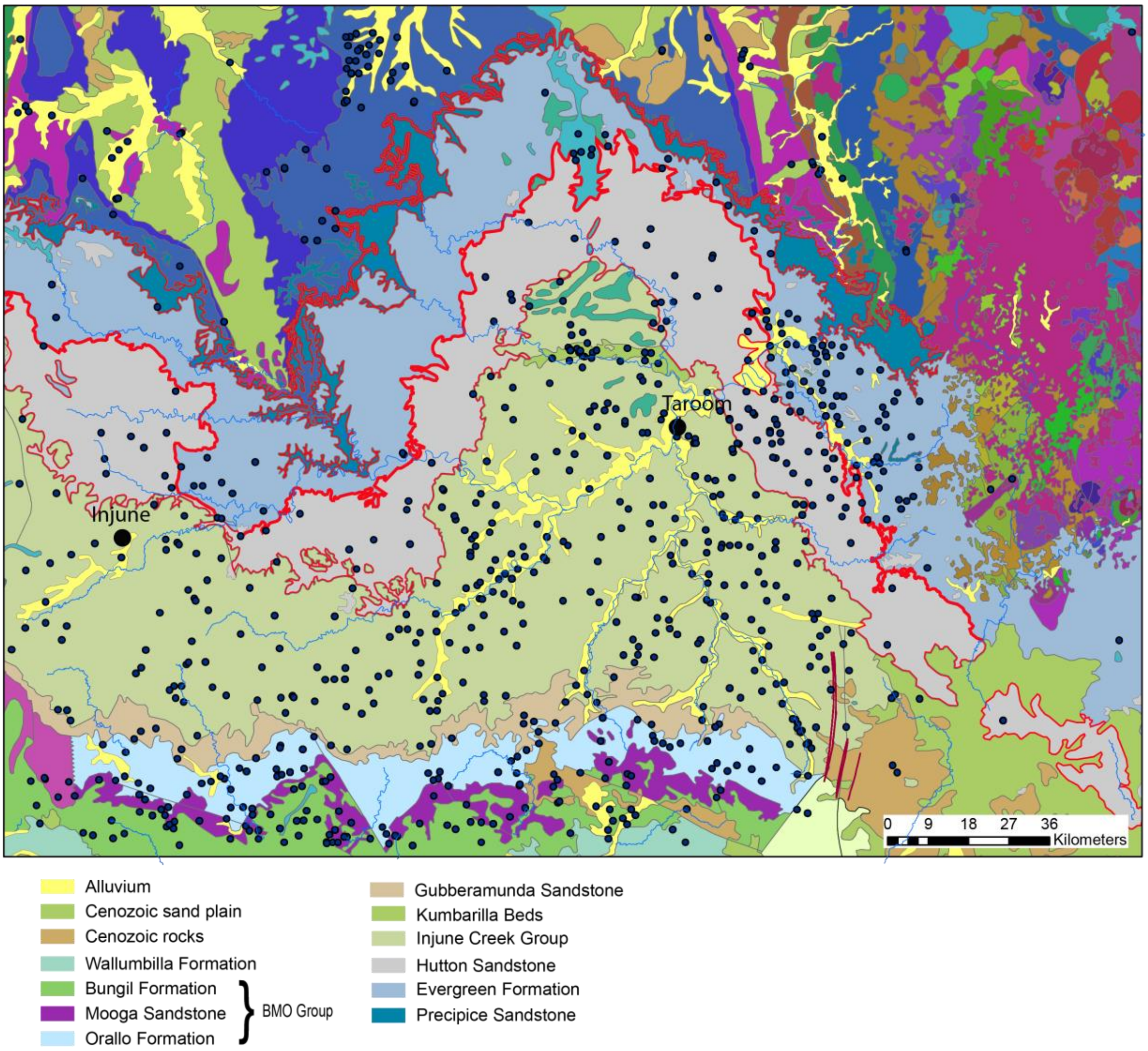

Figure 6 Groundwater bore locations with hydrochemical records in aquifers in the northern Surat Basin (DNRM, 2016)

The assessment of hydrochemical patterns, recharge estimation and the creation of potentiometric surface maps depend on a reliable assignment of screened aquifer intervals to a particular stratigraphic formation (Mallants et al., 2016). The quality of the groundwater bore data is highly variable, and bore-aquifer assignments and screen information are sometimes incomplete or incorrect, as confirmed by importing the screen intervals into 3D geological models. An essential part of this project therefore consisted of data quality control checks on stratigraphic data (which are not available for all groundwater bores) and the assignment of the screened aquifer for each bore. Although for the development of groundwater flow models it sometimes is a common practice to assign a bore to multiple aquifers or take a 'best guess' on the screened formation where no bore construction details exists (e.g. assume that the bore is screened only in the formation in which it terminates), this is not possible for a water chemistry or isotope baseline assessment.

There are many challenges associated with the task of assigning bores to aquifers, particularly as many of the groundwater bores in the Surat Basin were constructed decades ago and as bore construction details are missing or are incomplete (Mallants et al., 2016). One of the key challenges is that the stratigraphy along the bore depth profile is unknown for many bores in the DNRM groundwater database (DNRM, 2016). Furthermore, where stratigraphic data exist, these are often incorrect or exist only for part of the bore depth profile. The depth of bores is also unknown for a substantial number of bores, as are the top and/or bottom of the screened interval. The 'aquifer table' within the DNRM groundwater database only lists the aquifer at slightly more than 50% of the bores for which hydrochemical data exists, and these groundwater database bore assignments are sometimes incorrect or incomplete, as confirmed by the comparison with the 3D geological models. Where the depth of the screened interval (e.g. hypothetical example bore 1 in Figure 4) or the bore depth are unknown, hydrochemical data or environmental tracers cannot be included in the hydrochemical or tracer assessment as it is not possible to assign an aquifer with high confidence.

To verify the data from the DNRM groundwater database, two 3D geological models from the Office of Groundwater Impact Assessment (OGIA) (Office of Groundwater Impact Assessment, 2016) and CSIRO (Raiber, unpublished) were used, allowing to independently confirm the formation at the screened interval. For this purpose, the screened intervals were imported into the 3D geological models using Gocad/SKUA software™ (Paradigm Geophysical Pty Ltd), and the models were then queried to identify the formation where the bores are screened. The use of the 3D geological model helped considerably to improve the confidence in aquifer assignments. Where this procedure indicated that a bore is only screened in one aquifer (e.g. hypothetical example bore 2 in Figure 4), the hydrochemical data were included in the hydrochemical assessment. However, the assessment also confirmed that many bores are screened across different formations (e.g. hypothetical example bore 3 in Figure 4), and data from these bores can also not be used for the hydrochemical assessment as it cannot be determined from which aquifer the water is sourced. Furthermore, as for all models, the 3D geological models are subject to uncertainties resulting for example from interpolation of widely-spaced data (e.g. Raiber et al., 2012). In areas where many bores with reliable stratigraphic data exist (e.g. in areas where exploration for coal seam gas has occurred), the uncertainty of the aquifer assignments based on the 3D geological models is considered low. In contrast, in other areas such as for example close to the outcrop beds of the Hutton Sandstone, Evergreen Formation and Precipice Sandstone in the northern part of the Mimosa Syncline, there are only few exploration bores and only a small number of groundwater bores with stratigraphic data; the uncertainty of bore-aquifer assessments is therefore higher in these areas. This indicates a considerable knowledge gap and should be addressed in future studies, e.g. by using geophysical wireline logging instruments to ascertain the screened formation of bores in these areas.

2.2. Groundwater chemistry data

Groundwater chemistry data from the Queensland DNRM groundwater database (DNRM, 2016) for the period 1976 to May 2016 were included in the hydrochemical assessment. Prior to 1976, potassium, a major ion, was often not measured. Data for the hydrochemical assessment were compiled from multiple sources:

- DNRM groundwater database and DNRM groundwater chemistry baseline survey
- GISERA W4 sampling (Suckow et al., 2016)
- GISERA W6 sampling (this study)
- Geoscience Australia (Geoscience Australia 2014; Ransley et al., 2015)
- Geoscience Australia (Feitz et al. 2014)
- Coal Seam Gas company monitoring data (QGC, Santos and Origin Energy)
- OGIA groundwater – surface water sampling campaign (OGIA 2017)

2.3 Multi-variate statistical analysis

Hierarchical Cluster Analysis (HCA) is a multivariate statistical technique commonly adopted in groundwater hydrochemical studies to identify patterns within a dataset to enhance the understanding of physical and chemical processes that underpin groundwater evolution (e.g. Stetzenbach et al., 1999; Güler et al., 2002; Menció and Mas-Pla, 2008; Daughney et al., 2010; Raiber et al., 2012). Many variables should ideally be used in an HCA to enable an accurate depiction of groundwater chemistry and the processes that control it. In this study, ten variables were selected, namely, pH, Ca, Mg, Na, K, HCO_3, Cl, F, SO_4 and electrical conductivity. Prior to the multi-variate statistical analysis, data quality control checks were performed on all hydrochemical records. Sampling records where charge balances were outside ± 10% or where the aquifer at the screened interval was unknown were excluded from further analysis. A charge balance cut-off of ±10% was used instead of the commonly used ±5% to ensure that only sites where severe charge imbalances occur are excluded, as suggested by Guggenmos et al. (2011) and Güler et al. (2002). Such severe charge balance imbalances can arise for example from incorrect data entries or missing values for major ions. Values below detection limit were replaced with the detection limit, as previously described and explained in other studies elsewhere (e.g. Farnham et al. (2002) and Raiber et al. (2012)). Although dissolved methane concentrations were not included in the HCA, they were used for the interpretation on the hydrochemical evolution within the Hutton Sandstone and Precipice Sandstone.

With the exception of pH, all variables were log-transformed to ensure that they conform to a normal distribution before the multivariate statistical analysis was conducted. The HCA presented in this work was carried out using the StatGraphics Centurion software (Manugistics Inc., USA). Two linkage rules were adopted, following the methodology described by Daughney et al. (2010) and Raiber et al. (2012): (1) the nearest neighbour rule for identifying sites with significantly different hydrochemical signatures to recognize outliers that are placed as residuals in a separate group; and, (2) the Ward's rule for generating distinct clusters based on an analysis of variance used to group all non-residuals into separate clusters. Similarities across all variables were assessed using the square of the Euclidean distance (E). The transformed input data along with linkage rules and the similarity measure are considered as the most appropriate techniques for classifying hydrochemical data (Güler et al., 2002; Daughney et al., 2010; Raiber et al., 2012). The outcome of this process is a dendrogram (Cloutier et al., 2008).

As it involves an element of judgment when determining the suitable number of clusters that are representative of a sample population, HCA is considered a semi-objective technique. In this study, the dendrogram was visually inspected, and then the centroid concentrations (represented by the median) for different input variables and clusters at different separation thresholds were compared (Cloutier et al., 2008; Raiber et al., 2012). The median was preferred as a better indicator of central tendency compared to the mean as it is less sensitive to extreme values (Helsel and Hirsch, 2002).

3 Results and discussions

3.1 Hydrochemical variability within the Dawson River catchment (all aquifers)

A multivariate statistical analysis of the hydrochemical data was conducted on hydrochemical data from all aquifers within the Dawson River catchment to assess the variability within each aquifer and determine if there are similarities or characteristic differences between different aquifers. A cross-tabulation was conducted to determine if there is a statistical relationship between aquifer membership and the HCA-derived cluster (Figure 7). A hypothesis test was conducted to determine whether to reject the hypothesis that the 'aquifer membership' and 'cluster membership' classifications are independent. This test showed that the P-value is less than 0.05, and the hypothesis that the observed value of 'aquifer membership' for a case is independent from its value for 'cluster membership' can therefore be rejected at the 95% confidence level. In other words, statistically 'aquifer membership' and cluster membership are mutually dependent.

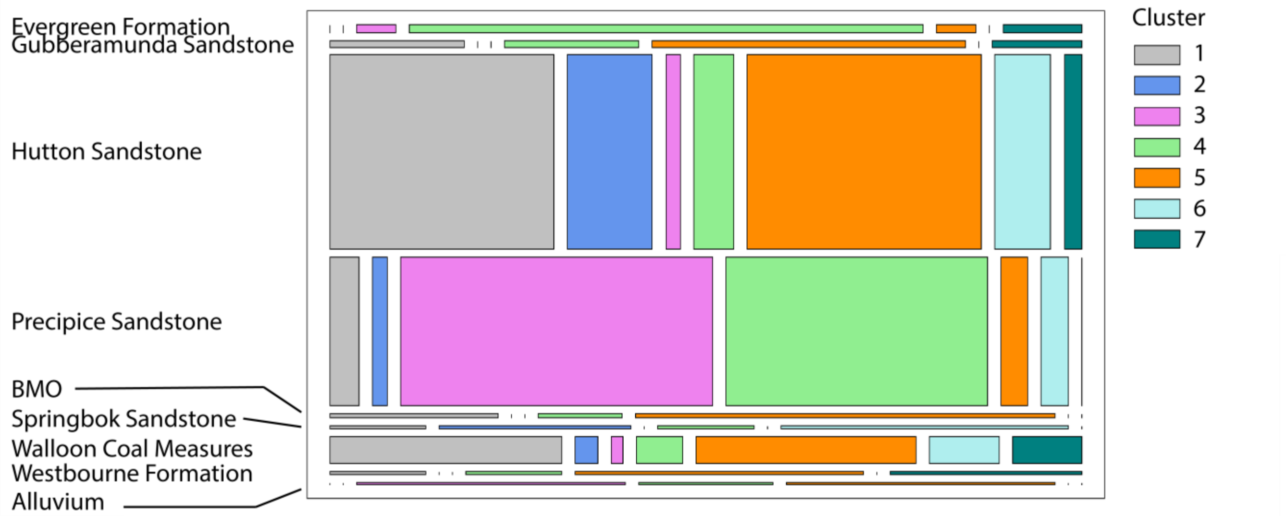

Figure 7 Aquifer cluster membership of all major aquifers in the Dawson River catchment in the northern Surat Basin. The width of the bars represents the relative percentage of groundwater records assigned. The height is proportional to the number of existing hydrochemical records for each formation (e.g. a large number exists for the Hutton Sandstone, whereas only a small number of records are available for the Springbok Sandstone).

The multivariate statistical analysis of the hydrochemistry of all groundwaters within the Dawson River catchment in the Surat Basin showed that hydrochemical records of all aquifers are assigned to multiple clusters, indicating that hydrochemical variability occurs within all aquifers (Table 1). The HCA and cross-tabulation also show that the hydrochemistry of the Precipice Sandstone and Hutton Sandstone are very distinct, as most of the Hutton Sandstone groundwaters are assigned to clusters 1 and 5, whereas most Precipice Sandstone groundwaters are assigned to clusters 3 and 4. As previously suggested by Mallants et al. (2016), groundwater chemistry within the Walloon Coal Measures and the Hutton Sandstone appears to be similar in the northern Surat Basin (although the dataset used in this study does not include hydrochemical records from the

Walloon Coal Measures production waters and therefore represents the shallower parts of the aquifer).

Table 1 Median concentrations of hydrochemical parameters for the seven groundwater chemistry clusters of all groundwaters in the Dawson River catchment in the northern Surat Basin

	Cluster 1	Cluster 2	Cluster 3	Cluster 4	Cluster 5	Cluster 6	Cluster 7
Counts of records	197	70	169	180	206	57	26
Percentage of all records	21.80%	7.70%	18.70%	19.90%	22.80%	6.30%	2.90%
EC (µS/cm)	1100	3445	204	319	2221	9651	1077
pH (mg/L)	8.58	8.35	7.3	6.89	8.07	7.55	7.5
Na (mg/L)	249	833	45	31	464	1668	229
K (mg/L)	1	4.85	2	3	2	8.7	1
Ca (mg/L)	2	4	1	19	19.2	208	3.5
Mg (mg/L)	1	1	0.4	9.85	2	57	1
HCO_3 (mg/L)	327	1342	110	146	431	504	352
Cl (mg/L)	130	560.5	9.5	20	461	3226	131
SO_4 (mg/L)	2	1.6	1	3	35.42	20	11
F (mg/L)	0.7	3.95	0.3	0.1	0.17	0.1	0.2
Ca/Na	0.008	0.005	0.022	0.613	0.041	0.125	0.015
Mg/Na	0.004	0.001	0.009	0.318	0.004	0.034	0.004
K/Na	0.004	0.006	0.044	0.097	0.004	0.005	0.004
Na/Cl	1.915	1.486	4.737	1.55	1.008	0.517	1.748
HCO3/Cl	2.515	2.394	11.663	7.308	0.936	0.156	2.687
SO4/Cl	0.015	0.003	0.105	0.155	0.077	0.006	0.084
F/Cl	0.00540	0.00700	0.03160	0.00500	0.00040	0.00003	0.00150

The ion ratio plots (Figure 8) confirm that there are significant overlaps in ion/chloride ratios between different aquifers. The comparison of ion-chloride ratios relative to the ratios of seawater (Drever, 1997) and the average-weighted ratios of rainfall at the two closest rainfall stations (Charleville and Toowoomba (Crosbie et al., 2012)) shows that there are significant changes with increasing salinity. Generally, the freshest groundwaters within all aquifers are characterised by high ratios of major cations relative to chloride (Figure 8), and the excess ions relative to local precipitation are likely supplied by the dissolution of primary silicate minerals or ion exchange within the rocks. Ion/Cl ratios (e.g. K/Cl, Ca/Cl and Mg/Cl) rapidly decrease at approximately 1000–2000 µS/cm to values close to or below those in local rainfall and the ratio of seawater. This either suggests an increase in chloride or that some of the weathering-derived ions are removed from solution rapidly, e.g. via adsorption on clay mineral surfaces. For Na/Cl and HCO_3/Cl, the ratios also decrease with increasing salinity, although at slightly higher salinities than for the other major ions. Furthermore, there is likely to be calcite and dolomite precipitation, as indicated by saturation indices in some groundwater in exceedance of where calcite and dolomite precipitation typically occurs. This suggests that calcite and dolomite precipitation has removed some Ca, Mg and HCO_3 from the groundwater. As a result, groundwater become more Na-Cl dominated. In studies elsewhere in Australia, it was also suggested that the removal of cations can be facilitated by preferential uptake of ions by vegetation in the recharge area (Edwards and Webb, 2009).

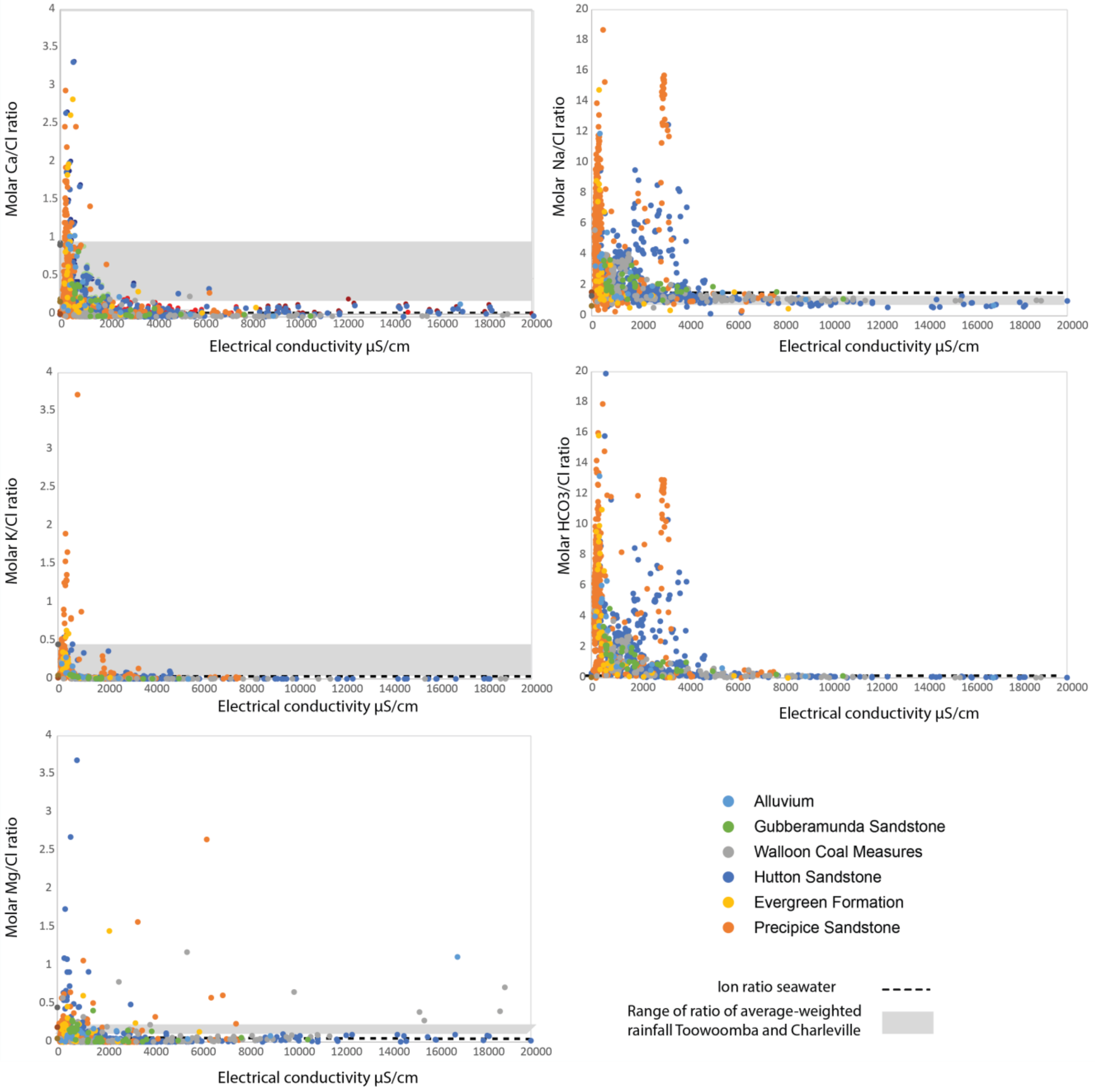

Figure 8 Ion/Cl versus electrical conductivity plots for groundwater in selected major aquifers within the Dawson River catchment in the northern Surat Basin. Rainfall ion ratios are based on Crosbie et al. (2012).

Relationships between Cl and Br can provide valuable insights into the source of salinity in groundwater (e.g. Cartwright et al., 2004). Within the hydrochemical dataset of the northern Surat Basin, 210 measurements of groundwater bromide concentrations are available (for all aquifers); the molar Cl/Br ratios of these groundwaters range from ~170 to ~1800 at all except two sites, with these two outliers having higher ratios (approximately 2300 and 4100, respectively). As shown in Figure 9, the Cl/Br ratios of most groundwaters are above the ratio of seawater of 650 (Davis et al., 1998, 2001), and there are no systematic variations with salinity. Rainfall Br concentrations in Brisbane, Toowoomba and Charleville were generally below detection limit (0.05 mg/L; Crosbie et al., 2012), and groundwater Cl/Br ratios could therefore not be compared with local rainfall Cl/Br ratio. However, Cartwright et al. (2004) suggested that coastal rainfall commonly has a similar Cl/Br ratio as seawater, whereas inland rainfall, particularly in arid or semi-arid climates, has lower Cl/Br ratios due to the preferential removal of NaCl in early rainfall near coastal areas. This was also confirmed by Davis et al. (1998, 2001), who showed that fresh groundwater in the USA is characterised by decreasing Cl/Br ratios from 400 near the coast to <150 in the continental interior. The measured Cl/Br ratios in the groundwaters of the northern Surat Basin are considerably less than what would be expected of brines or from the dissolution of halite (10,000–100,000) (Cartwright et al., 2004), confirming a meteoric (or cyclic) rainfall source of dissolved salts. The slightly elevated Cl/Br ratios relative to the oceanic ratio may suggest that there is an additional minor contribution from windblown dust, as observed in other areas of Australia. However, $^{87}Sr/^{86}Sr$ ratios (Feitz et al., 2014; Raiber & Suckow, unpublished data) confirm that this possible contribution is likely to be very minor, as the $^{87}Sr/^{86}Sr$ ratios would otherwise be much higher than those observed, due to the higher $^{87}Sr/^{86}Sr$ ratios in central Australia where most windblown dust originates.

Specific hydrochemical processes that control these observed patterns are discussed in detail in Sections 3.2 and 3.3 for the Precipice Sandstone and Hutton Sandstone, respectively.

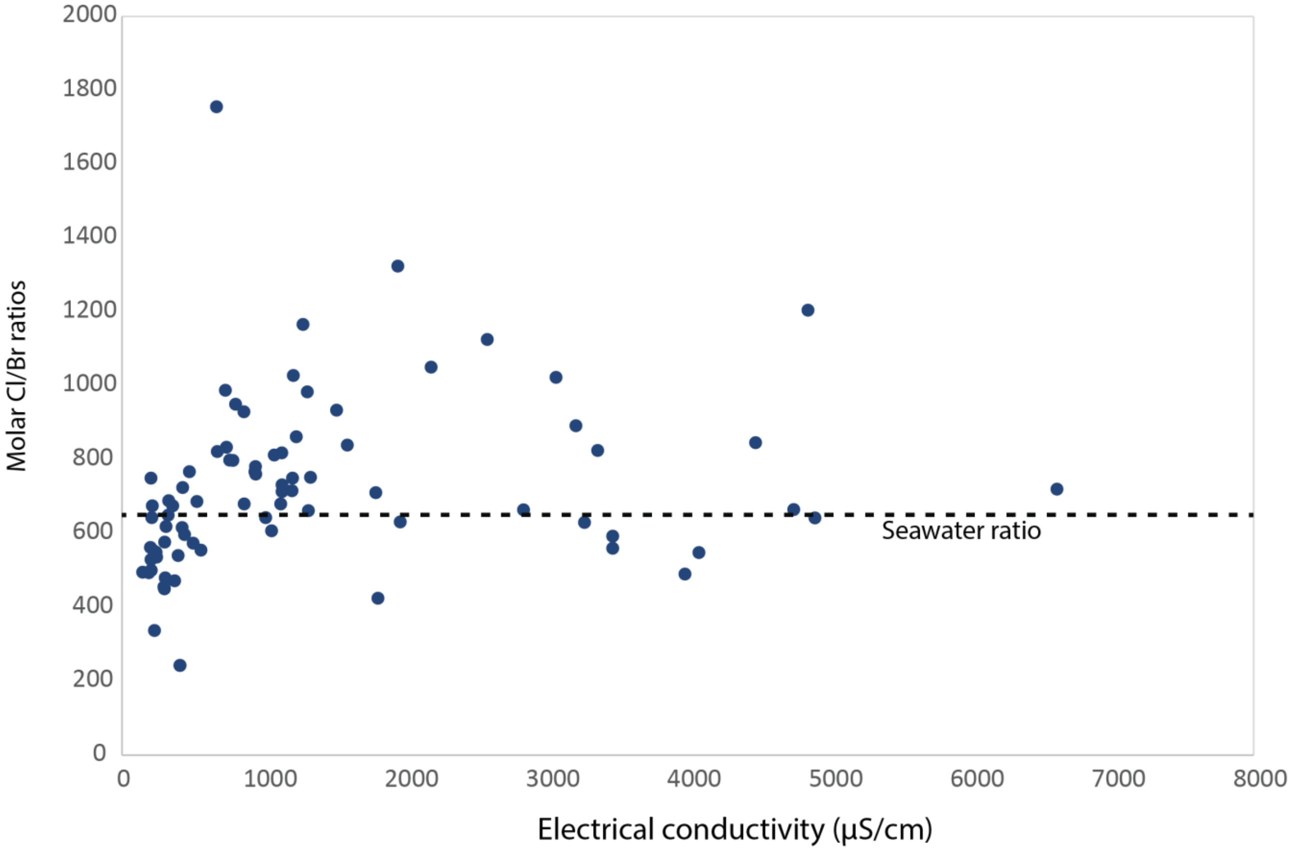

Figure 9 Molar chloride-bromide ratios versus electrical conductivity in all aquifers within the northern Surat Basin.

3.2 Hydrochemical variability within the Precipice Sandstone

To further refine the understanding of hydrochemical variability and their controls within the Precipice Sandstone, a key agricultural aquifer within the northern Surat Basin, a HCA was conducted on all hydrochemical records of bores screened within this unit. The salinity of groundwaters within the Precipice Sandstone in the northern Surat Basin ranges from very fresh (<300 µS/cm) to brackish (~5000 µS/cm) (Table 2). The HCA revealed five clusters within the dataset (Table 2), all marked by differences in pH, electrical conductivity or relative ion ratios. They will be discussed in the following text for different 'hydrochemical zones' where differences could be observed. The hydrochemical clusters each include groundwater hydrochemical records with similar characteristics. The hydrochemical zones are defined qualitatively to discuss the spatial variability of groundwater chemistry and hydrochemical cluster-membership. They represent geographical areas within the study area where certain hydrochemical patterns are observed (e.g. a consistent assignment of many groundwaters to a single cluster, or conversely, a highly variable groundwater hydrochemistry marked by assignment of groundwater hydrochemical records to multiple clusters in the same area).

Table 2 Hierarchical Cluster Analysis of Precipice Sandstone groundwaters, median ion concentrations, ion ratios and dissolved methane concentrations of identified clusters (methane concentrations were not included in the HCA)

	Cluster 1	Cluster 2	Cluster 3	Cluster 4	Cluster 5
Counts of records	122	55	36	23	73
Percentage of all records	39.50%	17.8%	11.65%	7.45%	23.6%
EC (µS/cm)	194.5	373	379	2345	257
pH (mg/L)	7.3	7.23	8.19	8.23	6.6
Na (mg/L)	39.25	38	84.5	555	25
K (mg/L)	2	4	3	3	2
Ca (mg/L)	1.05	20	1	14	18
Mg (mg/L)	0.3	7	1	1.5	10
HCO_3 (mg/L)	96.75	140	194.89	677	143.7
Cl (mg/L)	9.35	18	20	353	16
SO_4 (mg/L)	1	15	1	34	1
F (mg/L)	0.2	0.1	0.95	0.3	0.1
Ca/Na	0.027	0.526	0.012	0.025	0.720
Mg/Na	0.008	0.184	0.012	0.003	0.4
K/Na	0.051	0.105	0.036	0.005	0.080
Na/Cl	4.198	2.11	4.225	1.657	1.563

HCO3/Cl	10.348	7.778	9.745	2.019	8.981
SO4/Cl	0.107	0.833	0.05	0.101	0.063
F/Cl	0.02140	0.00560	0.04750	0.00090	0.00630
Methane (µg/L)	3370 (34)	774 (25)	2085 (31)	3055 (5)	1420 (48)

3.1.1 Major characteristics of hydrochemical clusters in the Precipice Sandstone

Cluster 1: Groundwaters in the Precipice Sandstone assigned to Cluster 1 have very low salinities (median EC of 194 µS/cm). Of all clusters, groundwaters in this hydrochemical group have the highest median HCO_3/Cl ratios, and have very high Na-Cl ratios (Figure 10, Table 2), and are therefore classified as Na-HCO_3 waters. This cluster has low median concentrations of sulfate (mostly at the detection limit) and Ca, and the lowest Mg concentrations of all clusters. The Ca/Cl and Mg/Cl ratios of most samples within this groundwater chemistry group are below the ratios of local rainfall (Figure 10). Groundwaters assigned to this cluster have the highest median methane concentration (3370 µg/L, based on 34 measurements) (Table 2; Figure 11). Groundwaters assigned to this cluster occur primarily in the hydrochemical zones 1 and 2 (Figure 12).

Cluster 2: Groundwaters assigned to Cluster 2 have slightly higher salinities than Cluster 2 (373 µS/cm), but are still very fresh. They are also dominated by Na and HCO_3, but have considerably higher Ca, Mg and SO_4 concentrations than Cluster 1 groundwaters, and this cluster has the highest median concentrations of K, with many samples within this cluster having K/Cl ratios above those of local rainfall (Figure 10). Groundwaters within this cluster have a median methane concentration of 774 µg/L (based on 25 measurements) (Table 2; Figure 11). Groundwaters assigned to Cluster 2 are observed in hydrochemical zones 2, 3 and 4 (in the latter zone, the bores are located close to the Burunga Leichhardt Fault (Figure 12).

Cluster 3: Groundwaters assigned to Cluster 3 have a similar median salinity as Cluster 2 (379 µS/cm), but have considerably higher Na concentrations, with all samples in this cluster exceeding the Na/Cl ratio of local rainfall and seawater (Figure 10). Ca and Mg concentrations of groundwaters in this cluster are very low, and mostly below the ratio of local rainfall and seawater. Likewise, SO_4 concentrations are low (lowest SO_4/Cl ratio of all clusters). In contrast, fluoride concentrations of groundwaters within this cluster are high (median concentration of 0.95 mg/L) and methane concentrations are 2085 µg/L (Table 2; Figure 11). Groundwaters assigned to this cluster occur primarily in hydrochemistry zones 4 and 5 (Figure 12).

Cluster 4: Groundwaters assigned to Cluster 4 have substantially higher salinities (median EC of ~2350 µS/cm; Table 2). Na and HCO_3 are the dominant ions, but Cl are also considerably higher than in other clusters. Most groundwaters in this cluster have Ca/Cl ratios below those of local rainfall and more similar to those of seawater. Mg/Cl ratios are substantially below those of local rainfall and seawater. K/Cl ratios are very similar to those of seawater (Figure 10), and the median methane concentration is 3055 µS/cm (although based on only five measurements) (Table 2;

Figure 11). Groundwater chemistry samples assigned to this cluster occur primarily in hydrochemistry zone 6, but can be found locally throughout the northern Surat Basin (Figure 12).

Cluster 5: Groundwaters assigned to Cluster 5 have the second lowest median salinities (257 µS/cm) (Table 2). They have high Ca and Mg concentrations (and thus, high Ca/Cl and Mg/Cl ratios, which are generally above the ratio of seawater and mostly higher than those of local rainfall; Figure 10). K/Cl ratios are low (Figure 10), and SO_4 concentrations are also low. The median methane concentration of this cluster is 1420 (based on 48 samples; Table 2 and Figure 11). Groundwaters assigned to this cluster almost exclusively occur in hydrochemistry zone 3 (Figure 12).

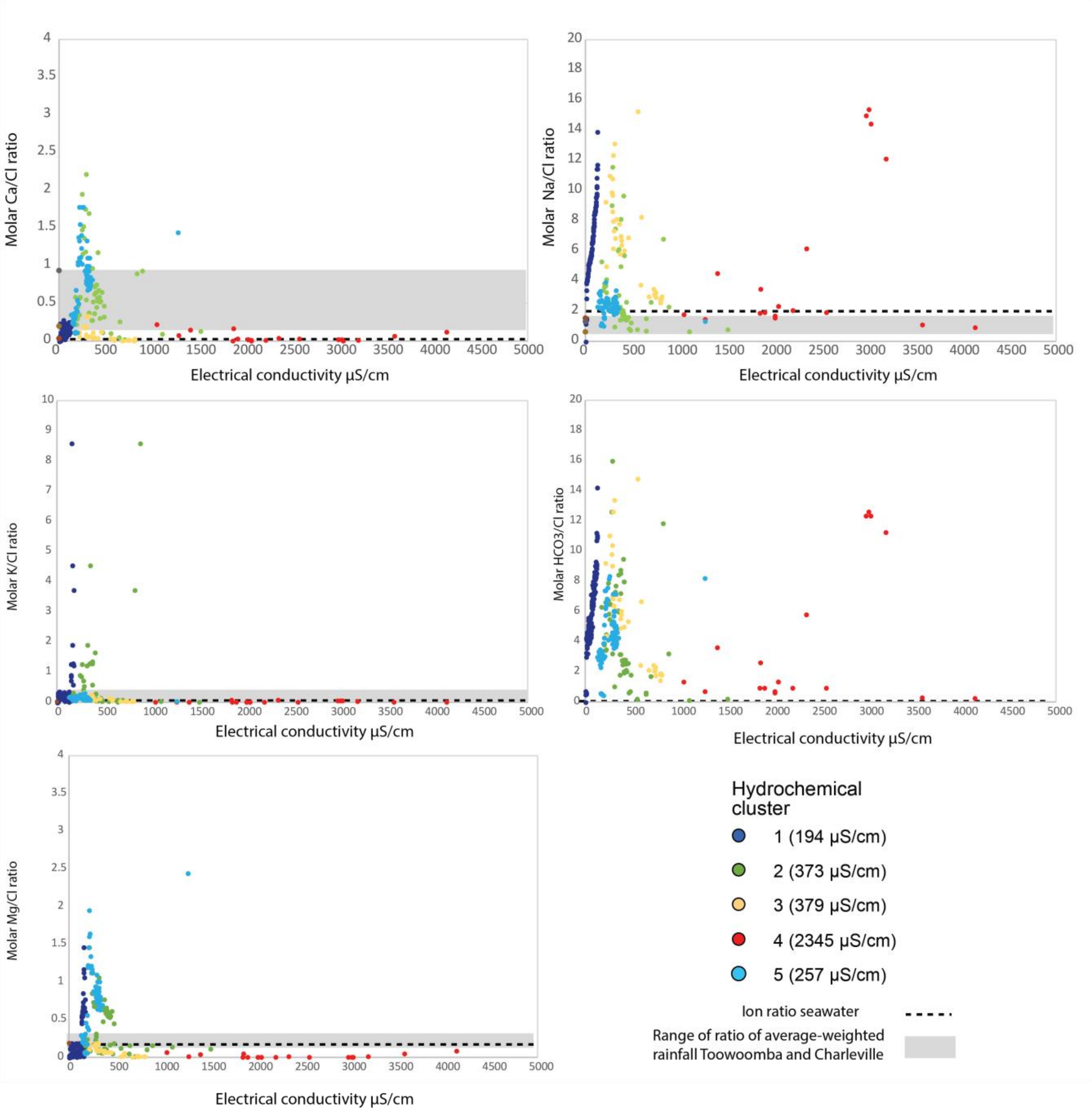

Figure 10 Ion/Cl versus electrical conductivity plots and cluster-membership for groundwaters in Precipice Sandstone groundwaters within the Dawson River catchment in the northern Surat Basin. Rainfall ion ratios are based on Crosbie et al. (2012).

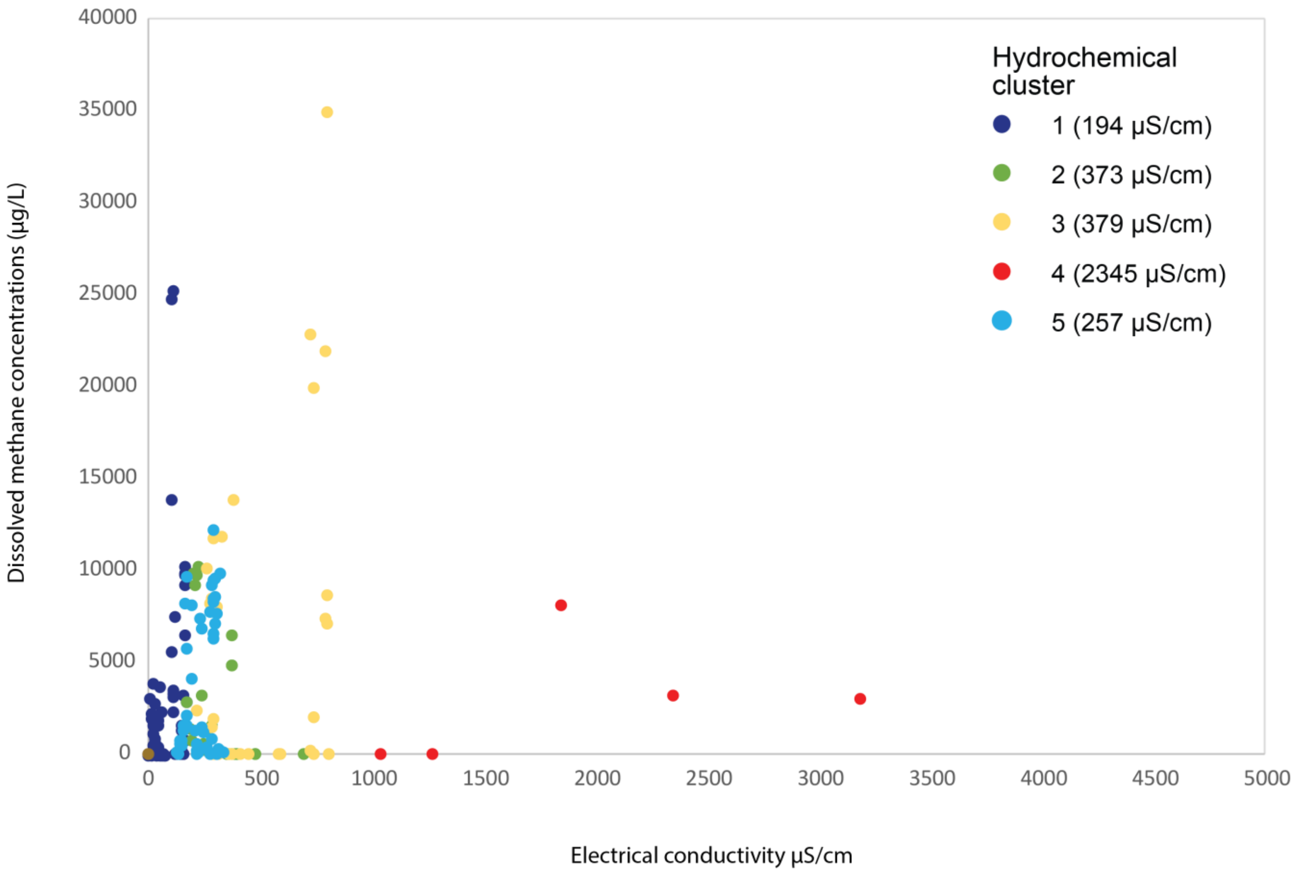

Figure 11 Methane concentrations in Precipice Sandstone groundwaters versus electrical conductivity (relative to hydrochemical cluster).

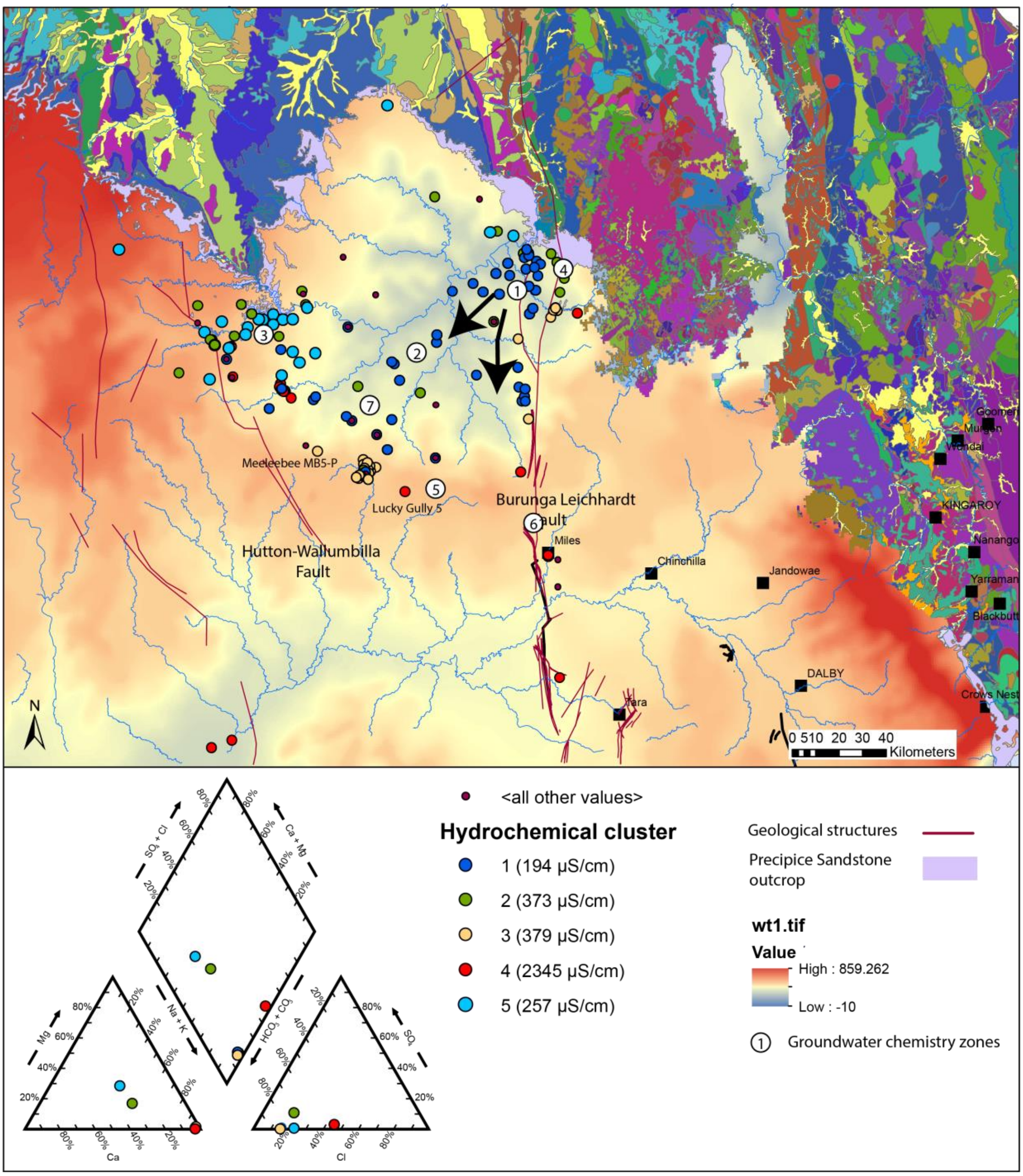

Figure 12 Spatial distribution of HCA-derived cluster membership of groundwaters in the Precipice Sandstone. The inset Piper plot shows the median concentrations of each cluster. The potentiometric surface map (for entire Great Artesian Basin) is based on Ransley and Smerdon (2012)

3.3 Hydrochemical variability within the Hutton Sandstone

The multivariate statistical analysis showed that there are seven hydrochemical groups (clusters) within the Hutton Sandstone in the northern Surat Basin. The different clusters are marked by differences in pH, electrical conductivity or ion ratios.

3.3.1 Major characteristics of hydrochemical clusters in the Hutton Sandstone

The major characteristics of each cluster are described below and the spatial context will then be discussed in the following text for different 'hydrochemical zones' (defined in Section 3.2) where differences could be observed. In comparison to the Precipice Sandstone, the hydrochemistry of the Hutton Sandstone in the northern Surat Basin is much more variable, with median electrical conductivities of the seven clusters ranging from 431 µS/cm to 11,000 µS/cm (Table 3), indicating that the lithological composition of the Hutton Sandstone is much more variable than that of the Precipice Sandstone.

Cluster 1: Groundwaters assigned to Cluster 1 have a median electrical conductivity of 1150 µS/cm. This cluster has low median Ca, Mg and K concentrations, with most groundwaters assigned to this cluster showing molar ion/Cl ratios for these parameters below those of local rainfall and close to or below those of seawater (Figure 13) and low SO_4 concentration (mostly at or close to the detection limit). In contrast, Na and HCO_3 versus Cl ratios are high and mostly above the ratios of local rainfall and seawater (Figure 13). Fluoride concentrations are high (median of 0.8 mg/L), and this cluster has the second highest median methane concentrations of all clusters (6160 µg/L; Table 3 and Figure 14). Groundwaters assigned to this cluster primarily occur in hydrochemistry zones 1 and 2 (Figure 15).

Cluster 2: Groundwaters assigned to Cluster 2 are brackish (electrical conductivity of 2000 µS/cm). These groundwaters are dominated by Na, HCO_3 and Cl. They have Ca/Cl concentrations similar to local rainfall and mostly above the ratio of seawater, but low Mg (mostly below the Mg/Cl ratio of local rainfall and similar to those of seawater) (Figure 13). Sulfate concentrations are clearly above the detection limit, and this cluster has low methane concentrations (median of 11 µg/L, based on 25 samples; Table 3, Figure 14). Groundwaters assigned to this cluster occur close to, but mostly outside, the outcrops of the Hutton Sandstone (Figure 15).

Cluster 3: Groundwaters assigned to Cluster 3 have low electrical conductivities (median of 947 µS/cm), and are dominated by Na, HCO_3 and Cl. Groundwaters within this cluster are characterised by low median Ca, Mg and K concentrations (with ion/Cl ratios below those of local rainfall and similar or below those of seawater, Figure 13). Sulfate concentrations are moderate and fluoride concentrations are low (Table 3). Methane concentrations are low (median methane concentration of 17.5 µg/L based on 30 samples; Table 3 and Figure 14). Groundwaters assigned to this cluster primarily occur in hydrochemistry zones 3 and 4 in the north-western and central northern part of the northern Surat Basin (Figure 15).

Cluster 4: Groundwaters assigned to this cluster are brackish (median electrical conductivity of 3725 µS/cm) and dominated by Na and Cl. Ca concentrations are clearly measurable, but the ratios of Ca/Cl are lower than those of local rainfall, and similar to those of seawater (Figure 13). Mg concentrations are also mostly above detection limit, but the Mg/Cl ratios are low and generally below those of local rainfall. Na/Cl ratios are lower than those of seawater and very similar to the range of local rainfall (Figure 13). HCO_3/Cl ratios are low, and methane concentrations are also relatively low (median of 302 µS/cm; Figure 14 and Table 3). Groundwaters assigned to this cluster occur primarily in hydrochemistry zones 4, 5 and 6 in relatively close proximity to the outcrops of the Hutton Sandstone (Figure 15).

Cluster 5: Groundwaters assigned to Cluster 5 are considerably more saline than those of other clusters (median electrical conductivity of 11,000 µS/cm; Table 3). They have very high concentrations of Na and Cl. Ca and Mg concentrations are relatively high and generally above the detection limit. Their ratios relative to Cl are below those of local rainfall and very similar to those of seawater (Figure 13). Sulfate concentrations are clearly above the detection limit, and fluoride concentrations are low (mostly at the detection limit). Only two methane concentrations were measured for this cluster (Figure 14). Groundwaters assigned to this cluster occur in the north-eastern part of the northern Surat Basin (hydrochemistry zones 2, 6 and 7; Figure 15).

Cluster 6: Groundwaters assigned to this cluster have very low salinities (median electrical conductivity of 431 µS/cm; Table 3). Groundwaters of this cluster have high Ca, Mg and K concentrations (Table 3), and have the highest ratios of these cations relative to Cl (Figure 13), all of which are higher than those of seawater and many comparable or higher than those of local rainfall (Figure 14). Sulfate concentrations are mostly above the detection limit, and HCO_3/Cl ratios are high (Figure 15), and most measured methane concentrations are low (median of 16.5 µS/cm; Table 3 and Figure 13). Groundwaters assigned to this cluster occur almost exclusively in shallower parts of the basin within the outcrop beds of the Hutton Sandstone in hydrochemistry zones 8, 9 and 10 (Figure 15).

Cluster 7: Groundwaters assigned to Cluster 7 are brackish (median electrical conductivity of 2901 µS/cm; Table 3) and have very high Na and HCO_3 concentrations (with the ratios of both ions mostly above those of local rainfall and seawater; Figure 13). Ca and Mg concentrations are low and their ratios relative to Cl are below those of local rainfall and seawater (Figure 13). Similarly, the concentrations of SO_4 are very low (mostly at the detection limit), whereas fluoride concentrations are very high (median of 5 mg/L). Of all clusters in the Hutton Sandstone, this cluster has the highest median methane concentration (10,163 µS/cm based on 36 measurements), with most groundwaters containing considerable concentrations of dissolved methane (Figure 14). Groundwaters assigned to this cluster occur primarily in the deeper parts of the northern Surat Basin in hydrochemistry zones 11, 12 and 13 (Figure 15).

Table 3 Hierarchical Cluster Analysis of Hutton Sandstone groundwaters, median ion concentrations, ion ratios and dissolved methane concentrations (the latter were not included in the HCA)

	Cluster 1	Cluster 2	Cluster 3	Cluster 4	Cluster 5	Cluster 6	Cluster 7
Counts of records	145	107	53	64	35	50	58
Percentage of all records	28.30%	20.90%	10.30%	12.50%	6.80%	9.70%	11.30%
EC (µS/cm)	1150	2000	947	3725	11,000	431	2901
pH	8.6	7.8	8.7	7.8	7.6	7.2	8.4
Na (mg/L)	273	420	205	677	2050	51	747
K (mg/L)	1	2	1	4	9.1	2.7	4

Ca (mg/L)	2.2	13.1	3	50.15	262	29.1	3
Mg (mg/L)	1	1.15	1	7.4	115	8.1	1
HCO_3 (mg/L)	427	448	229	396	546	196	1169
Cl (mg/L)	135	401	159	949	3860	28.6	199
SO_4 (mg/L)	1	34.6	20	56	46	6.2	1
F (mg/L)	0.8	0.2	0.1	0.15	0.1	0.2	5
Ca/Na	0.008	0.031	0.015	0.074	0.128	0.571	0.004
Mg/Na	0.0036	0.0035	0.0048	0.011	0.056	0.159	0.001
K/Na	0.004	0.004	0.004	0.006	0.004	0.050	0.005
Na/Cl	2.022	1.047	1.289	0.713	0.531	1.786	3.756
HCO3/Cl	3.163	1.117	1.443	0.417	0.142	6.894	5.874
SO4/Cl	0.007	0.086	0.126	0.059	0.012	0.216	0.005
F/Cl	0.00593	0.00050	0.00063	0.00016	0.00003	0.00701	0.02513
Methane (µg/L)	6160	11	17.5	302	2590	16.5	10,163

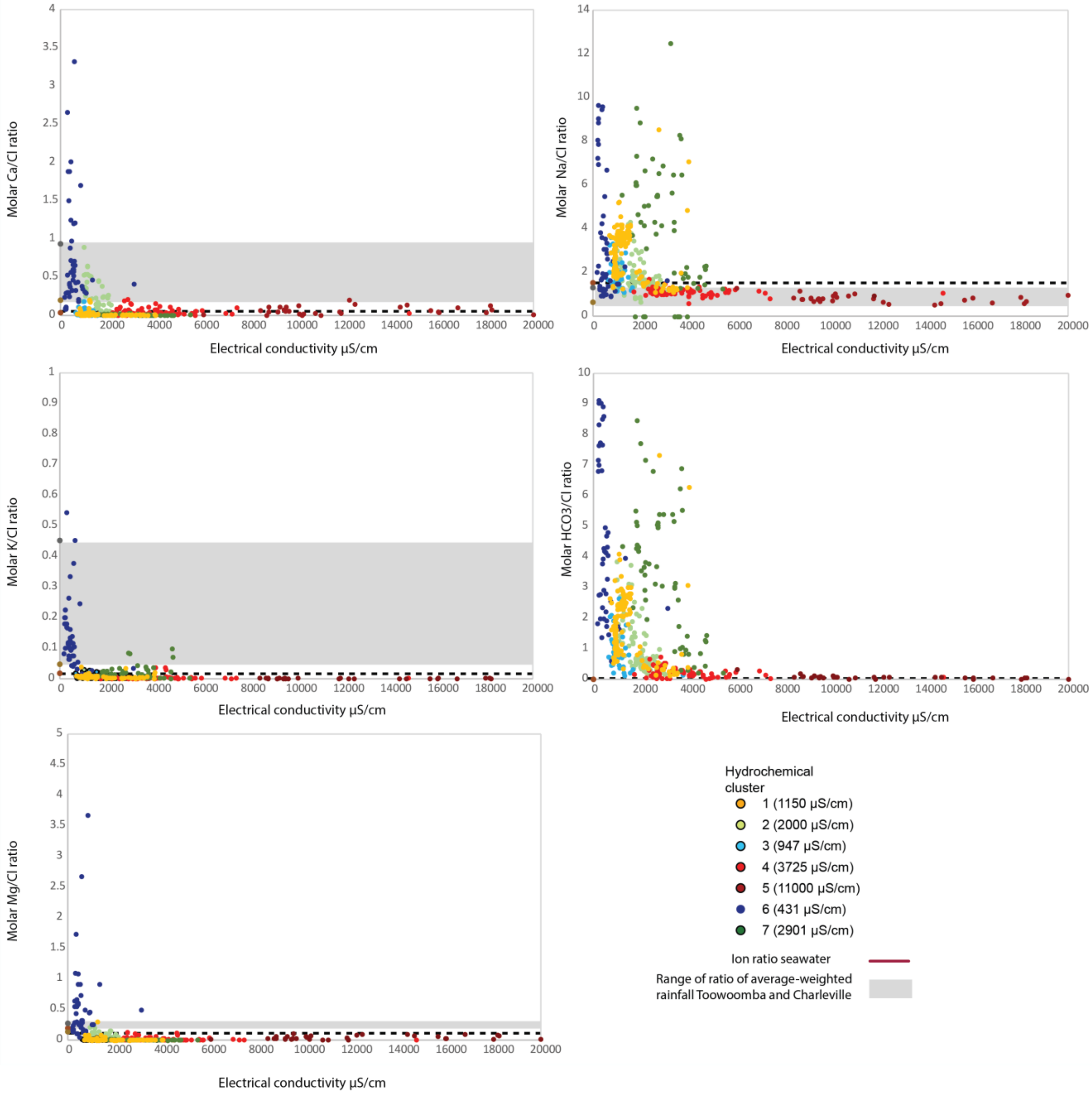

Figure 13 Ion/Cl versus electrical conductivity plots and cluster-membership for groundwaters in Hutton Sandstone groundwaters within the Dawson River catchment in the northern Surat Basin. Rainfall ion ratios are based on Crosbie et al. (2012).

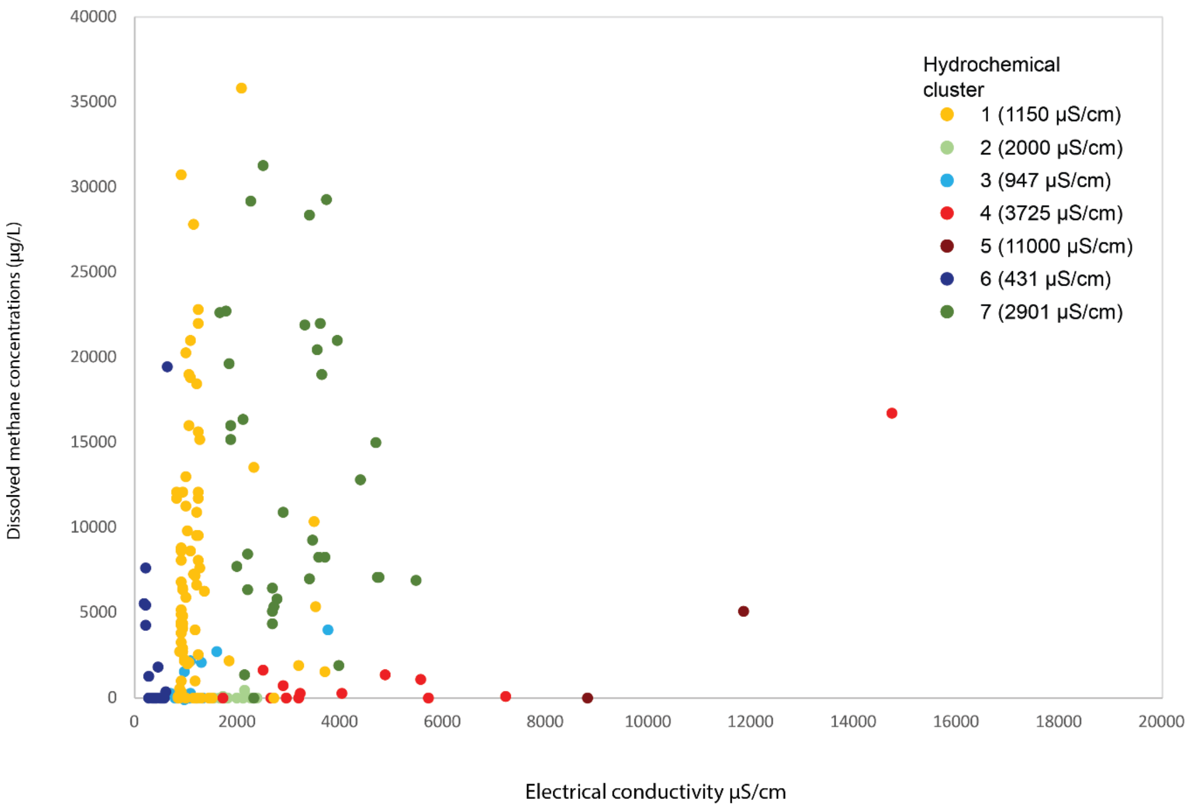

Figure 14 Dissolved methane concentrations of Hutton Sandstone groundwaters relative to electrical conductivity and hydrochemical cluster.

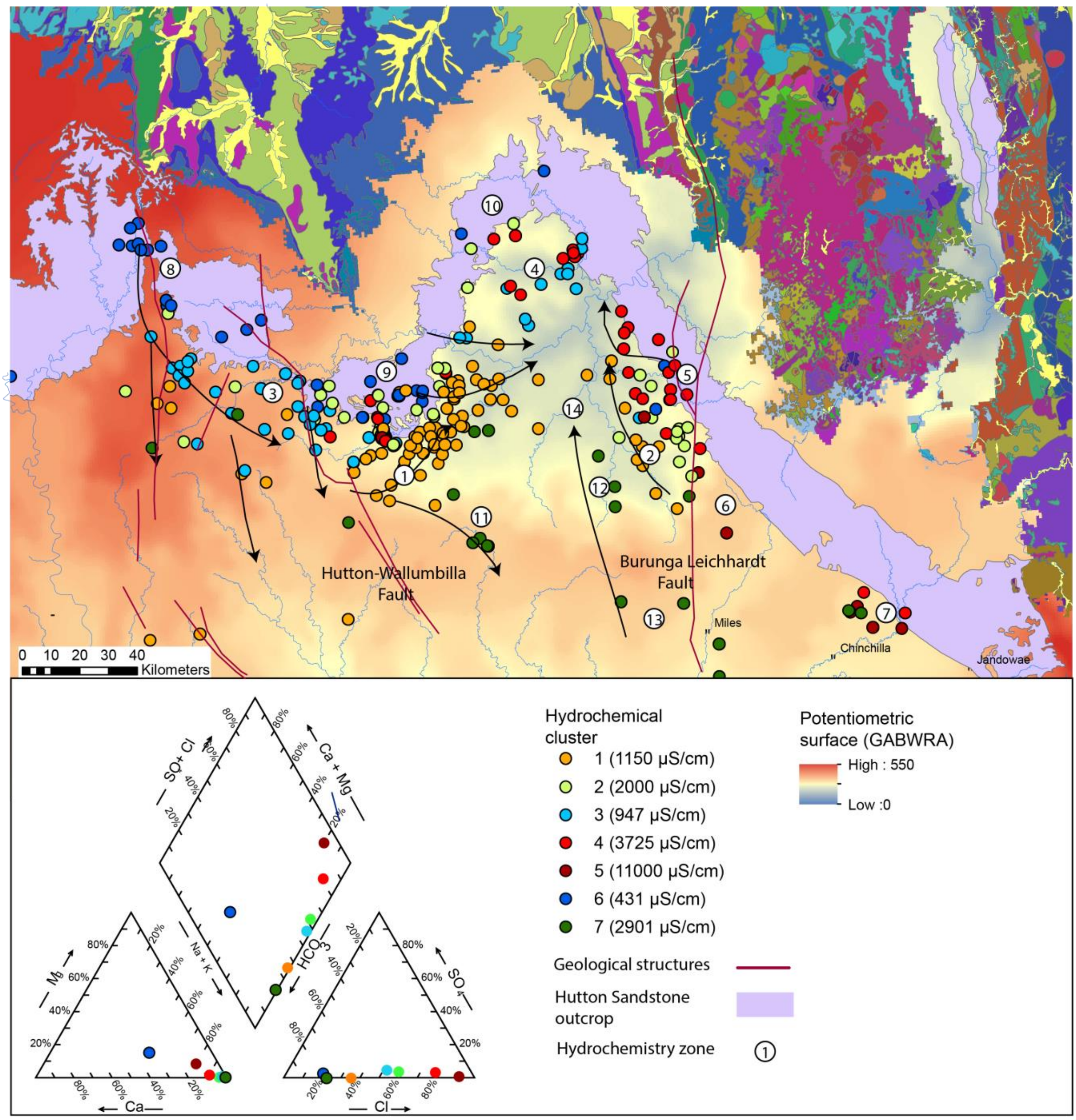

Figure 15 Spatial distribution of HCA-derived cluster membership of groundwaters in the Hutton Sandstone. The inset Piper plot shows the median concentrations of each cluster. The potentiometric surface map is based on Ransley and Smerdon (2012). Arrows indicate potential groundwater flow directions.

3.4 Hydrochemical evolution and implications for recharge processes

3.4.1 Precipice Sandstone

Groundwater chemistry data can be used to assess the hydrochemical evolution of groundwaters. The major characteristics of the five groundwater chemistry clusters described for the Precipice Sandstone show that there are multiple processes that influence the hydrochemical evolution of these groundwaters.

At low salinities, many of the groundwaters have ion/Cl ratios higher than those of seawater or local rainfall (Figure 10), attributed to silicate dissolution or ion exchange. However, with increasing salinities, these ion/Cl ratios commonly fall below those of seawater or local rainfall (Figure 10), suggesting that the weathering-derived ions are removed from solution by adsorption on clay mineral surfaces. Most of the hydrochemical clusters identified for the Precipice Sandstone have similar electrical conductivities but somewhat different ions/Cl ratios. Many of the characteristics observed for the Precipice Sandstone groundwaters are also commonly described for groundwaters that have interacted with coal seams, including the low SO_4, Mg, Ca concentrations and high Na and HCO_3 concentrations (e.g. Van Voast, 2003; Mallants et al., 2016). However, despite some similar hydrochemical characteristics, the Precipice Sandstone differs from overlying hydrostratigraphic units through its much lower electrical conductivities than adjacent aquifers, and somewhat similar hydrochemical characteristics do not mean that there is any hydraulic connection with coal seams, as many of these characteristics are not unique to coal seams but can form independently in other aquifers with proceeding hydrochemical evolution through processes such as methanogenesis. Although elevated methane concentrations are often primarily associated with groundwaters interacting with coal seams (e.g. Papendick et al., 2011), methane was also observed in many groundwaters within the Precipice Sandstone, and Ransley et al. (2015) suggested that most groundwaters in the Great Artesian Basin outside the recharge area contain some methane. Furthermore, the Precipice Sandstone is also recognised as the major commercial conventional petroleum reservoir in the Surat Basin, with oil and gas primarily trapped by geological structures, and sealed by the mudstones of the overlying Evergreen Formation (Randall 2013; Office of Groundwater Impact Assessment, 2016a). Previous work suggested that the methane in the Precipice Sandstone is of thermogenic origin (Feitz et al., 2014), whereas methane in the Walloon Coal Measures was described as a mixture of biogenic and thermogenic methane (Ransley et al., 2015).

The increase in HCO_3 is also commonly attributed as a control of precipitation of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), which can lead to a reduction of the concentrations of Ca and Mg (Van Voast, 2003).

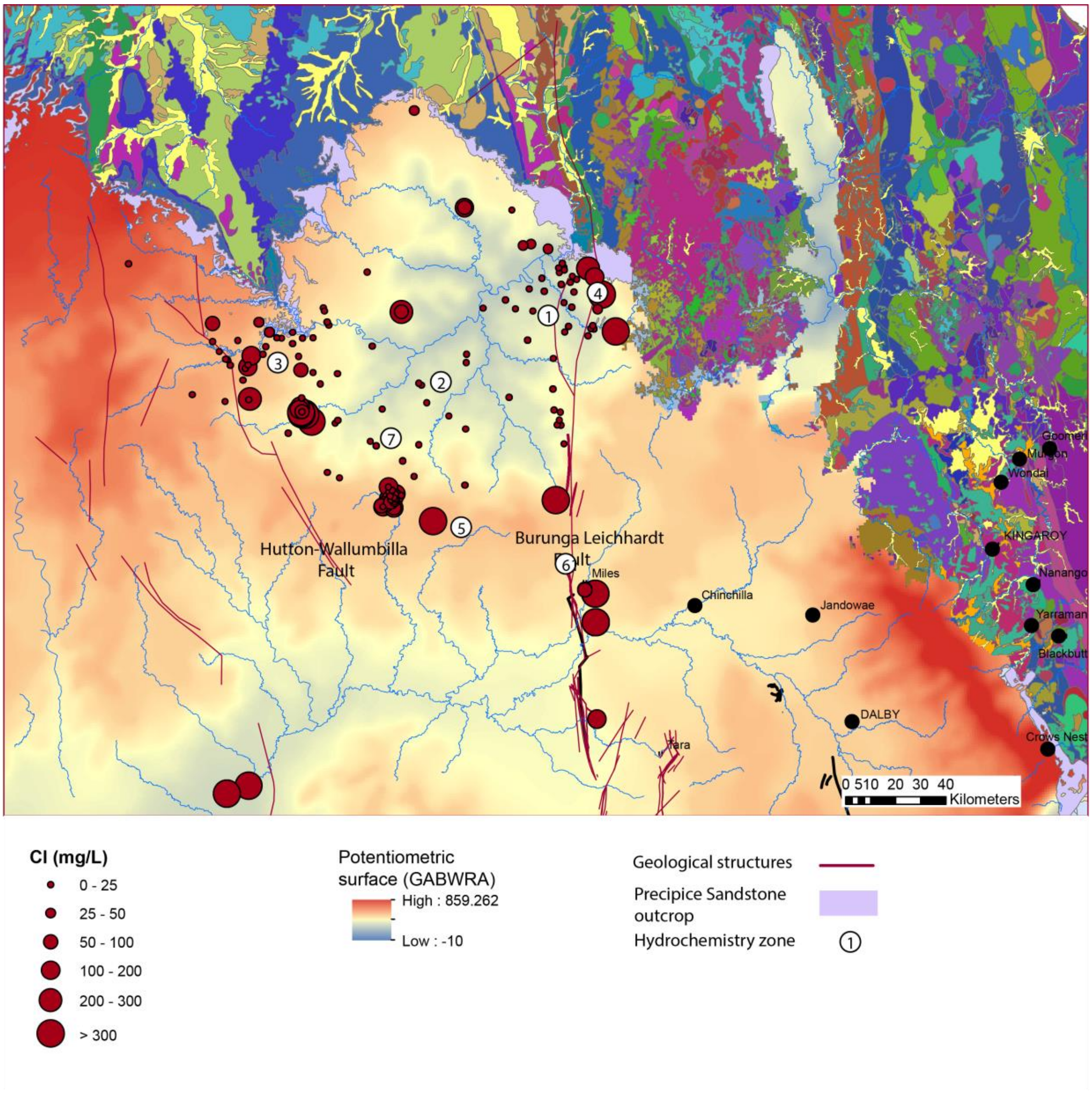

Figure 16 Spatial distribution of groundwater chloride concentrations in the Precipice Sandstone. The Potentiometric surface map is based on Ransley and Smerdon (2012).

Amongst the Precipice Sandstone groundwaters, groundwater hydrochemical records assigned to clusters 1 and 5 most closely resemble recharge waters, as they are sourced from close proximity to the outcrop beds of this unit and show some of the characteristics of groundwaters within or near recharge areas (e.g. their often high ion/Cl ratios). However, other characteristics such as their low SO_4 concentrations and measured methane concentrations clearly above the detection limit indicate that some hydrochemical evolution has already occurred. As shown on Figure 12, there are considerable spatial gaps in hydrochemical data for the Precipice Sandstone. For example, there are no groundwater hydrochemical records within the outcrop beds of the Precipice Sandstone available for assessment, suggesting that the freshest unevolved groundwater chemistry signatures are likely not captured by this dataset, and there are only a limited number of hydrochemical records in the deeper parts of the Surat Basin in the south. This limits the usefulness of hydrochemistry to determine groundwater flow paths. However, some initial conclusions can nevertheless be drawn. For example, groundwater chloride concentrations in hydrochemistry zone 2 (mostly Cluster 1) tend to be slightly lower than those in hydrochemistry zone 1 (although groundwaters in both zones have low Cl concentrations, as shown in Figure 16). Many of the groundwaters in hydrochemistry zone 3 also are assigned to Cluster 1 and have similarly low Cl concentrations, suggesting that a significant component of groundwater in hydrochemistry zone 3 may be recharged in zone 2. The presence of groundwaters assigned to Cluster 4 (Figure 12) and the elevated Cl concentrations (Figure 16) indicate that the Burunga Leichhardt Fault may form a pathway for interactions between the Precipice Sandstone and overlying units. This could be further tested through the collection of additional groundwater chemistry samples and analysis for environmental tracers.

3.4.2 Hutton Sandstone

Similar to the Precipice Sandstone, many different hydrochemical processes can be observed within the Hutton Sandstone based on the HCA and the groundwater ion/Cl ratios relative to local rainfall, allowing to infer how groundwater evolution progresses in the northern Surat Basin. In contrast to the Precipice Sandstone, Hutton Sandstone groundwaters show a much wider spectrum of hydrochemical evolution. In contrast to the Precipice Sandstone, hydrochemical records from within the outcrop area are available for the Hutton Sandstone (Cluster 6 groundwaters in hydrochemical zones 8, 9 and 10; Figure 15). Groundwaters assigned to this cluster show the characteristics of ‘recharge waters’ such as their elevated ion/Cl ratios (compared to local rainfall and seawater ratios). Furthermore, unlike groundwaters within the Precipice Sandstone groundwater chemistry clusters 1 and 5, this Hutton Sandstone groundwater chemistry cluster lacks any signs of progressing groundwater evolution such as low SO_4 concentrations, and most (but not all) groundwaters have methane concentration close to the detection/reporting limit. This suggest that these groundwaters indeed represent the start of flow paths, and that recharge rates to the Hutton Sandstone ae high in this area.

Interestingly, although many groundwaters in hydrochemical zone 5 occur within or near the recharge area, many of these groundwaters are assigned to Cluster 4, which contains groundwaters with high Cl concentrations (Figure 17) and ion/Cl ratios indicating that these groundwaters are considerably more evolved, as previously also observed by Underschultz and Vink (2015). This indicates that recharge rates here are low, possibly reflecting a different lithological composition of the Hutton Sandstone in this area compared to the Hutton Sandstone at the western flanks of the Mimosa Syncline. As for the Precipice Sandstone, there are also groundwater samples that contain considerable amounts of dissolved methane within the Hutton Sandstone, and in particular samples assigned to clusters 1 and 7 (Figure 14). Groundwaters assigned to these cluster also show many of the attributes commonly associated with coal seam gas groundwaters previously described in this report, and previously described for the Walloon Coal Measures in this area (Mallants et al., 2016).

The relative good spatial distribution of groundwater chemistry records within the Hutton Sandstone in the northern Surat Basin allows to draw some conclusion of possible, likely or unlikely groundwater flow paths. As indicated, groundwater recharge occurs in hydrochemical zones 8, 9 and 10, and groundwater then for example flows towards hydrochemical zones 1 and 3 (Figure 15 and Figure 17). A northerly groundwater flow direction similar to flow path 1 (Figure 2) can also not be ruled out based on the hydrochemistry. It is likely that there is a considerable degree of mixing in hydrochemistry zone 1, including a flow contribution from hydrochemical zones 3 and 9.

Based on the hydrochemistry, a northerly groundwater flow direction similar to flow path 2 within the Hutton Sandstone from hydrochemical zone 12 towards zone 13 and 14 is possible, although there is overall a poor data point density in this central area of the Mimosa Syncline (Figure 15 and Figure 17). In contrast, a significant groundwater flow component from hydrochemical zone 2 towards hydrochemical zone 12 is unlikely based on the hydrochemical data, as this would require a down-gradient decrease of the chloride concentration (Figure 17), which is unlikely given the commonly assumed conservative nature of Cl (e.g. Appello and Postma, 2006). Furthermore, if this was the case, then a considerable increase of the Cl concentrations between hydrochemical zones 13 to 14 would be expected.

In the northern part of the Mimosa Syncline (hydrochemistry zone 4; Figure 15), the hydrochemistry shows no distinct pattern, and fresh and brackish groundwaters are interspersed. This could indicate several things: it could for example mean that recharge from hydrochemistry zone 10 and the eastern outcrop beds to this deeper part is relatively minor. This could indicate that much of the infiltrating groundwater discharges rapidly into the Dawson River and its tributaries rather than contributing towards deep recharge as suggested by other authors based on the present-day potentiometric surface map (e.g. Ransley et al., 2015; Office of Groundwater Impact Assessment, 2016). Another possible explanation is that there are various recharge sources and complex mixing patterns; the presence of relatively saline and evolved groundwaters despite the proximity to the recharge area could also mean that groundwater flow is localised and possibly stagnant in some areas within the aquifer.

Unlike for the Precipice Sandstone, there is no indication from the hydrochemistry that the Burunga Leichhardt Fault acts as a preferential pathway for aquifer interactions. However, it is important to note that there are only few bores with hydrochemical records located along this fault in the southern part near Miles (Figure 17).

Overall, the hydrochemical assessment of the Hutton Sandstone suggest that groundwater recharge and flow patterns in the northern Surat Basin are complex. The observed patterns are consistent with present-day potentiometric surface maps (see Section 1). However, based on the available data, a southern flow component can also not be excluded in some areas.

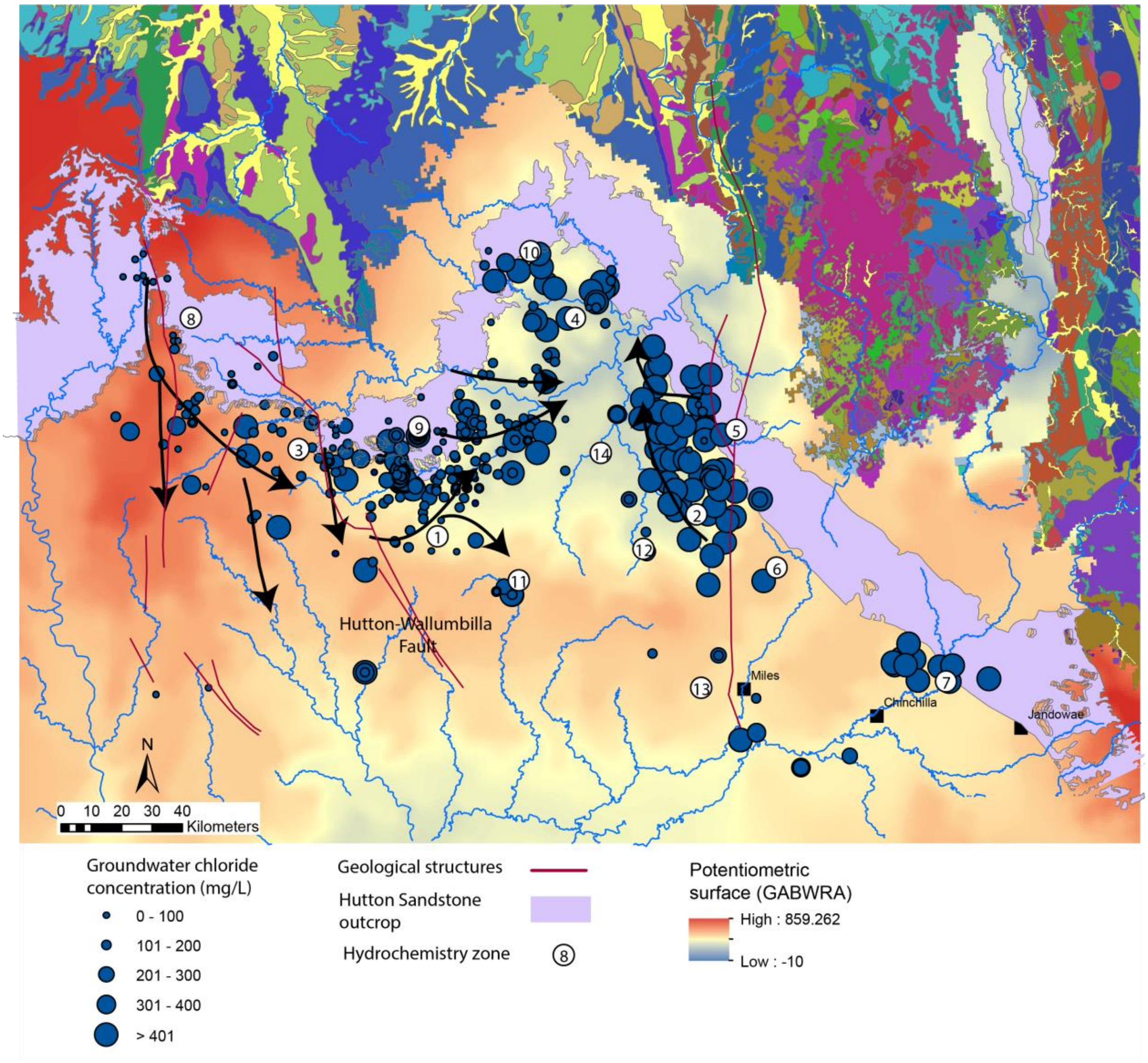

Figure 17 Spatial distribution of chloride concentrations of groundwaters in the Hutton Sandstone. The potentiometric surface map is based on Ransley and Smerdon (2012).

3.5 Limitations and future steps

The spatial representations of the groundwater chemistry records within the Precipice Sandstone and Hutton Sandstone highlights that there are not enough groundwater chemistry data within or near the aquifer outcrop areas and not enough bores with hydrochemical data in the deeper parts of the Surat Basin. To assess the hydrochemical evolution in sedimentary basins, the hydrochemical changes occurring from the outcrop beds (and inferred recharge areas) to the deeper parts of the sedimentary basin should be evaluated. The lack of hydrochemical records in outcrops and deeper parts of the northern Surat Basin means that these endmembers are not well-characterised in this part of the Surat Basin.

Where possible and where bores exist, future work should therefore focus particularly on the outcrop areas and on the central part of the Mimosa syncline (as already partly followed by the sampling campaign in this project). Furthermore, there are limited surface water chemistry data available to allow characterising the potential interactions between the aquifers of the northern Surat Basin and the Dawson River or its tributaries. Current efforts by the OGIA (e.g. OGIA, 2017) will help to improve the understanding on aquifer-surface water interactions in this area. Furthermore, the groundwater hydrochemistry data presented in this report could be integrated with spring hydrochemistry data to further improve the conceptual hydrogeological model of the Dawson River catchment.

The formation of methane in these aquifers or migration of methane into these aquifers can be assessed in more detail using methodologies as presented by Mallants et al. (2016) and where available, stable isotopes (δ^2H and δ^{13}C) of methane.

The similarities in hydrochemistry between the Hutton Sandstone and the Walloon Coal Measures observed in this study (Figure 7) and by Mallants et al. (2016) can also be further investigated. In these two studies, CSG production water hydrochemical records for the Walloon Coal Measures were not included, and the hydrochemical records for the Walloon Coal Measures therefore represent the shallower parts of the aquifer. Although these aquifers share an interface, similarities in hydrochemistry do not mean that there is any interaction between these aquifers, as hydrochemistry can evolve independently in different aquifers for example due to similar recharge processes or a similar lithological composition. To determine if there is any possible interaction, the similarities or differences of hydrochemistry in these two aquifers should be evaluated spatially; this could be further supplemented through the application of other environmental tracers to isotopically 'fingerprint' the groundwater in each aquifer (e.g. ^{87}Sr/^{86}Sr or the stable isotopes (δ^2H and δ^{13}C) of methane).

The hydrochemical approach applied in this project should also be extended to the eastern part of the Surat Basin; this would allow to further test/refine the whole-of-basin hydrodynamics and help to identify major data and knowledge gaps.

The influence of faults as potential pathways linking deeper and shallower formation could be further explored through the collection of samples for environmental tracers at multi-level monitoring sites. Although samples were already collected for the Hutton Sandstone and Precipice Sandstone by Suckow et al. (2016) and in this project, this could be extended to other aquifers at selected sites.

The bore aquifer assignment continues to be a considerable limitation for the hydrochemical assessments particularly near the recharge areas, where bores are widely spaced and where only few exploration bores exist. This issue could be addressed in future studies, e.g. by using geophysical wireline logging instruments to ascertain the screened formation of bores in these areas.

In the next step of this GISERA project, the data and knowledge from this report will be used to inform Task 4 of the project 'Constraining groundwater flow rates in the Surat Basin through environmental tracer and hydrochemical data'. This will involve reactive transport modelling and inverse geochemical modelling to quantitatively test different hypotheses on groundwater flow processes in the northern Surat Basin.

4 Conclusions

Hydrochemical data were used to assess the hydrochemical evolution and groundwater dynamics within the Dawson River catchment in the northern Surat Basin. The aim was to determine if there is a northerly groundwater flow component as suggested previously based on potentiometric surface developments.

The focus of this assessment were two key aquifers, the Hutton Sandstone and Precipice Sandstone, which are both extensively used for agricultural purposes and (in case of the Precipice Sandstone) as town water supplies. Prior to the hydrochemical assessment, extensive checks on the hydrostratigraphic unit at the screened interval were conducted to ensure that only hydrochemical records from bores where the screened aquifer is known were included in the assessment.

Following the data quality control checks, multivariate statistical techniques were used to identify patterns within the hydrochemical datasets. Median concentrations of the identified clusters were compared and the ratios of major ions relative to chloride in groundwater were compared with those in local rainfall to assess how groundwater evolution progresses within these aquifers. The hydrochemistry within the Precipice Sandstone is much more uniform than within the Hutton Sandstone. It also demonstrated that multiple processes influence the hydrochemical evolution of groundwater in these aquifers. Fresh groundwaters are primarily influenced by ion exchange and silicate dissolution, whereas more hydrochemically evolved groundwaters show signs of calcite and dolomite precipitation, sulfate reduction and methanogenesis. As indicated in previous studies, methane is present in both major aquifers investigated in this study. Whether this is produced in situ within these aquifers or has migrated from deeper formations could form part of future investigations.

The spatial assessment of the hydrochemistry allowed to draw several conclusions on groundwater flow paths, recharge processes and the influence of faults as pathways for aquifer connectivity. For example, several recharge areas within the Hutton and Precipice sandstone aquifers were identified. Some of the flow paths previously proposed based on potentiometric surface could not be excluded based on the hydrochemical evidence, whereas others were characterised as less likely. Elevated groundwater salinities within the Precipice Sandstone near the Burunga Leichhardt Fault that are considerably higher than in most other areas within this aquifer suggest that this fault may form a pathway that links this aquifer to over- or underlying units.

The assessment of hydrochemistry highlighted the value of baseline hydrochemical data. The project also highlighted the lack of hydrochemical data within the recharge areas and within the deeper parts of the Hutton Sandstone and particularly within the Precipice Sandstone in the northern Surat Basin as key knowledge gaps; further efforts to close these knowledge gaps could facilitate further improvement of the conceptual understanding of groundwater flow and hydrochemical evolution within these formations.

The hydrochemical assessment conducted in this component of the project will inform the next steps of this GISERA project, namely the reactive transport and inverse geochemical modelling.

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