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Groundwater flow and geochemical evolution in the Central Flinders Ranges, South Australia

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HIGHLIGHTS

- The groundwater flow and evolution were studied.
- Hydrogeological and hydrochemical methods were integrated successfully to improve and understand the hydrogeologic setting.
- The results confirmed recharge by rainfall infiltration as the main source of water.
- The conceptual model for recharge and flow is developed.

GRAPHICAL ABSTRACT

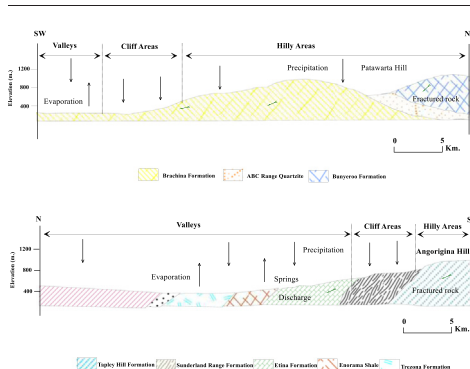


Fig. 1 Conceptual diagram of groundwater flow and evolution in the Oratunga Area

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ABSTRACT

The chemical characteristics of water in the Oratunga Area, Central Flinders Ranges, South Australia have been used to evaluate and determine the processes controlling water chemistry in addition to the sources of ions. The isotopic analysis results show that the groundwater is mainly meteoric. Based on the rock and water chemistry, ionic ratios, hydrochemical facies and saturation indices, the chemical evolution has been studied. The chemistry of groundwater revealed two types of water. Thus, in high topographic areas, low TDS, bicarbonate and mixed water types are dominated and support a rapid and direct recharge. While in the low topographic areas, high TDS and chloride compositions are the most common attributed to the accumulation of ions and groundwater evolution. Analysis of the ion concentration, head data and saturation indices shows a compositional trend that can be studied as an evolutionary system. The ionic ratios and hydrogeochemical modelling using NETPATH was used to quantify and verify the different hydrochemical processes. The resulting data shows that calcite dissolution/precipitation and cation exchange reactions are the major processes affecting groundwater chemical evolution of the groundwater in the basin. This study has provided a basis for a better understanding of the hydrogeologic setting in areas of a little data.

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1. Introduction

In arid and semi-arid areas, the scarcity and uncertainty of surface water supply makes groundwater an important part of the total water resource, and plays a useful role as water supply for drinking and

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irrigation (Tsujiyama et al., 2007; Keesari et al., 2014). In recent few years, use of groundwater resources has increased remarkably due to drought, the rapid growing of the worldwide economy, and an increase in the worldwide population (Llamas and Martínez-Santos, 2005). The over-use of groundwater has caused many severe problems such as salinization of groundwater, desertification, land salinization, and degeneration of vegetation (Ahmed et al., 2013; Lapworth et al., 2013). Therefore, the sustainable management of water and other environmental resources become an urgent issue worldwide.

Understanding the dynamics of the hydrogeological systems and identifying the hydrogeochemical evolution processes is required for the success of sustainable management experiences (Sophocleous, 2010; Eissa et al., 2014; Brkić et al., 2016). Along the flow-paths within the groundwater systems, the hydrochemical processes affecting the groundwater composition are different; dissolution dominates in the recharge area, ion exchange during the flow, while evaporation, precipitation and ion exchange dominate the discharge area in controlling groundwater chemistry (Tóth, 1999; Adams et al., 2001).

For arid regions, where evaporation dominates precipitation, the hydrogeochemical indicators have been effectively used for tracing the recharge sources and for quantifying the relative evaporation (Gárfias et al., 2010; Herczeg and Leaney, 2011; He et al., 2015; Wang et al., 2015). It has often been used to study the interactions of waters with rocks or sediments and to provide insights into aquifer heterogeneity and connectivity as well as the physical and chemical processes controlling water chemistry (Cartwright and Weaver, 2005; Wells and Price, 2015). In addition, it has been successfully used with isotopes as effective and economic tools in understanding the recharge and discharge of aquifer systems (Cartwright et al., 2006; Dogramaci et al., 2012). Geochemical modelling is used to quantify the geochemical reactions within groundwater systems (Hidalgo and Cruz-Sanjulián, 2001; Londoño et al., 2008; Eissa et al., 2013). The quantitative assessment of reactions in groundwater can be approached using the standard geochemical code, NETPATH-WIN (El-Kadi et al., 2011). Most of these studies focused

on areas of a large amount of data however, it remains unclear that whether it is feasible to use the available data to develop a reasonable model on which a sustainability plan for groundwater management can be developed.

In the Oratunga Area (Fig. 1), groundwater is the primary source for fresh water and plays a significant role in occupation and settlement. The region is dependent groundwater stored in fractured rock aquifers (Clark and Brake, 2009). Although the geology and stratigraphy of the bedrock have been studied in some detail (Preiss, 2000; Giddings et al., 2009; Backé et al., 2010; Fromhold and Wallace, 2012), little or nothing is known about the characteristics of groundwater. Therefore, the main objective of this research is to evaluate the dynamics of the groundwater in a limited data area in the Central Flinders Ranges, South Australia; the other aim is to investigate the presence of geochemical processes which would support the existence of different hydrodynamic conditions within the study area. All together directly affect the sustainable management of the water resources for this area.

2. Study area

The Oratunga Area is located in the Central Flinders Ranges, South Australia (Fig. 1). It is situated about 79 km. Southwest of Leigh Creek and 210 km north-east of Port Augusta. It is considered the topographically semi-closed basin. The study area includes about 341 km² in Central Flinders Ranges (Fig. 1). The central part has a relatively flat while the marginal areas are hilly and/or mountainous terrains.

The climate of the Flinders Ranges is described by (Schwerdtfeger and Curran, 1996) as arid to semi-arid. The winter rains are prolonged and gentle under low clouds from westerly air masses, while summer rains are brief, and intensely affected by northerly air masses (Schwerdtfeger and Curran, 1996). The average annual rainfall is 300 mm/year, and the mean monthly temperature varies from 16 °C (July) to 35 °C (January). In general, the slow and prolonged rainfall, cool to cold temperature and low

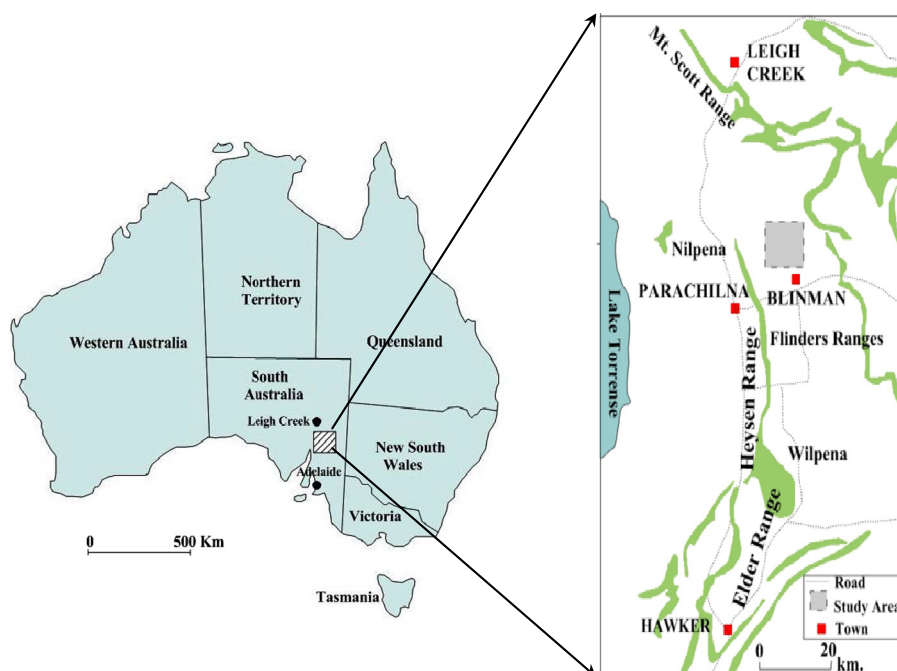


Fig. 1. Location map of the Oratunga Area in the Central Flinders Ranges.

evaporations during winter allows the infiltration and hence recharge to occur.

The study was conducted in a sparsely populated part of the Central Flinders Ranges nearby to the small town Blinman (population 100 approx). In the region, the most common land use is sheep grazing, and coal mining (NFRS, 2004). Skeletal to thin soil profiles of lithosol, calcic luvisol, calcic xersol, orthicsolonetz and chromic vertisol have developed on the underlying Neoproterozoic metasediments. The present day vegetation is a final product of the Gondwanic elements of the Australian flora which thrived after the Late Cretaceous/Early Tertiary separation of Australia and Antarctica and adapted to aridity during the Oligocene (Boomsma and Lewis, 1980). A low open woodland of native pine and black oak, or mallee bushland over seasonal grasses and small shrubs dominate the vegetation of the upland areas, whereas bluebush and saltbush communities or taller shrub lands common on the alluvial valleys and adjacent plains.

3. Geology and hydrogeology

Open to closely folded and refolded metasediments deposited during the Neoproterozoic and uplifted during the early Cambrian Delamerian Orogeny form the topographic skeleton of the Central Flinders Ranges Outcrops of stratigraphic sequences of the Neoproterozoic Burra Group, Umberatana Group and Wilpena Group are dominant (Fig. 2). In this area, only Umberatana and Wilpena Group rocks have been considered, depending on the field observation and the relationship to groundwater occurrences (Fig. 3). A number of studies have examined stratigraphy as well as the

geology of the study area (Preiss et al., 1998; Preiss, 2000; Williams et al., 2008; Giddings et al., 2009; Fromhold and Wallace, 2011; Gehling and Droser, 2012). In the Central Flinders Ranges, the sedimentary sequence is lesser in thickness and underwent more uplifting during the post-Delamerian Orogeny. The main tectonic structure in the Central Flinders Ranges is a series of tight to open, upright folds which were formed with NNW orientations, and faults and fractures trending NNE and ENE also formed during the earliest deformation event. This was followed by another event that led to major fault-propagation folds oriented ENE placed over folds to form a domal structure (Flöttmann et al., 1994; Flöttmann and Cockshell, 1996).

There have been no previous studies focused on the hydrogeology of the area. Much well drilling has been conducted throughout the Flinders Ranges in the course of mineral and hydrocarbon exploration. Although some of these wells have been drilled for groundwater, most of them are not in operation. This study shows that the hydrogeology follows closely the main geologic units. The sedimentary relationship of each unit is shown in (Figs. 3 and 4).

Groundwater generally occurs in semi-confined conditions and/or confined conditions may exist in places with the standing water levels (SWL) ranging from 1 to almost 20 m below land surface. Available data indicate that the groundwater occurs primarily in fractured rocks of the Tapley Hill, Etina, Brachina and Bunyeroo formations. The hydraulic conductivity for the rocks ranges from 1×10^{-4} – 1×10^{-6} m/d (Werner et al., 2014). Estimated well yields range from 0.5 to 1.5 l/s. No clear pattern of well yields in relation to rock type can be established.

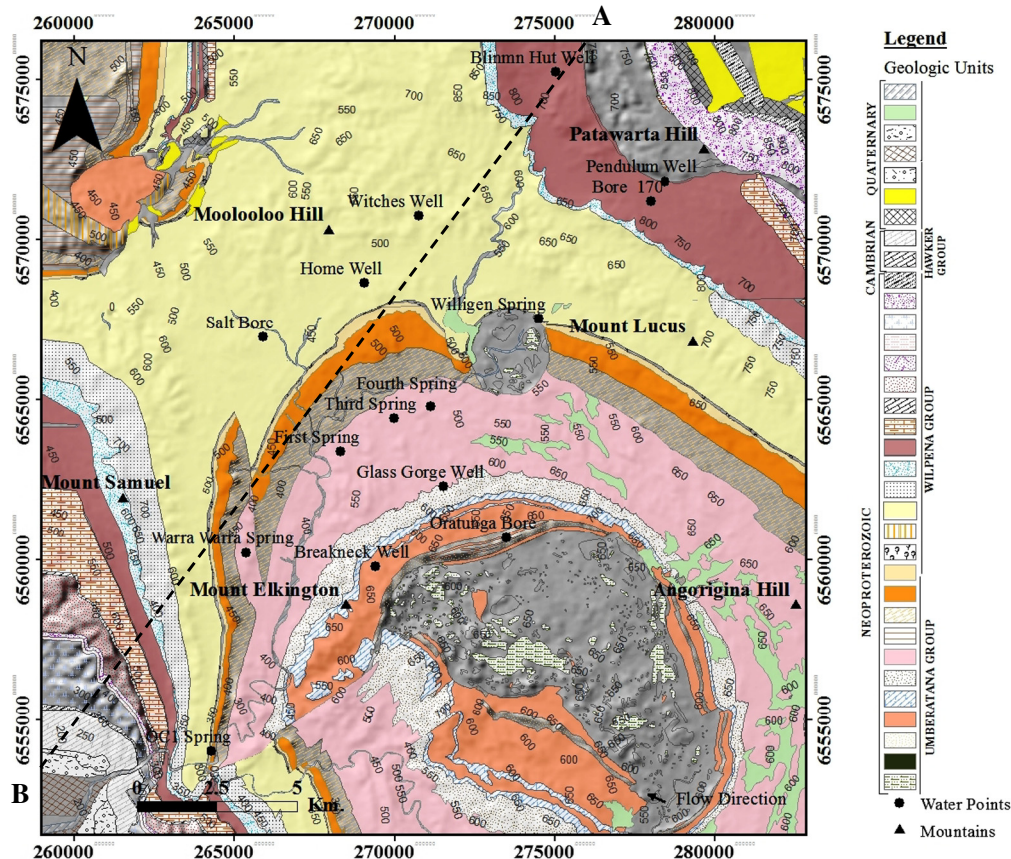


Fig. 2. Geological map of the study area showing the main stratigraphic features and distribution of water points (modified from map by Geological Survey of South Australia with the authority of Department for Manufacturing, Innovation, Trade, Resources and Energy).

| Sequence Sets | Lithostratigraphy | Lithological Log |
|-----------------------------|--|------------------|
| WILPENA GROUP | Wonoka Formation | |
| | Wearing Dolomite Member | |
| SANDISON SUBGROUP | Bunyeroo Formation | |
| | Wilcolo Sandstone Member | |
| | ABC Range Quartzite | |
| | Brachina Formation | |
| | Moorillah Siltstone Member Moolooloo Siltstone Member | |
| Nuccaleena Formation | | |
| UMBERATANA GROUP | Elatina Formation | |
| | Yaltipena Formation | |
| YERELINA SUBGROUP | Trezona Formation | |
| | Enorama Formation | |
| | Wundowie Limestone Member | |
| UPALINNA SUBGROUP | Etina Formation | |
| | Sunderland Formation | |
| | Wockerwirra Dolomite Member | |
| NEPOUTE SUBGROUP | Tapley Hill Formation | |
| | Mt. Caernarvon Greywacke Member Tindelpina Shale Member | |
| YUDNAMUTANA SUBGROUP | Wilyerpa Formation Warcowie Dolomite Member | |

Fig. 3. The main stratigraphic units in the Central Flinders area showing the main units from oldest to youngest (adapted from Giddings et al., 2009 and Gehling and Droser, 2012 and the field observation).

4. Materials and methods

A hydrogeological survey, water level measurements, hydrogeochemical and isotopic samplings and analysis were completed to achieve the objectives of this study. Surface water divides for the study area were delineated based on available topographical maps in a 1:50,000 scale. This was improved by means of 30-m resolution Shuttle Radar Topographic Mission (SRTM) images which allowed the determination of the altitude and location of water points. Water samples were then collected from wells and springs in May and September 2013. Parameters including temperature, pH and electrical conductivity (EC) were determined in situ using

Eutech digital portable meters in the field. Three samples were collected from each site and stored in washed plastic bottles for analysis of carbonate; chloride and other ions (Table 1).

The samples were stored at low temperature in a portable refrigerator. Major ion chemistry analysis was performed at the laboratory of the Australian Water Quality Centre (AWQC). The CaCO_3 content was determined as total alkalinity; HCO_3^- is measured by titration with 0.05 N HCl and methyl orange as the indicator. The concentration of Cl^- ions was determined by Automated Flow Colorimetry while the other elements were analyzed using ICP Spectrometry (ICP2). To compare seasonal variation of the groundwater recharge and evolution, Water level and EC of water in some wells were measured twice in every year from March 2008 to January 2013 and two samples were collected from Salt Bore one in May 2013 (almost the end of dry season) and the other in September 2013 (almost at the end of the major rainy season).

Eight samples were collected and sent for stable isotope analysis at the Commonwealth Scientific and Industrial Research Organisation (CSIRO) laboratory. Stable isotopes of water ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) were analyzed using a water equilibration system (WES) coupled to a PDZ Europa Geo 20–20 mass spectrometer and are reported relative to the international standard Vienna-Standard Mean Ocean Water (V-SMOW). Stable isotope values for the precipitation in the study area are not documented so a long-term measurement of precipitation at Adelaide Station (1962–1986) were obtained from the International Atomic Energy Agency's Global Network of Isotopes in Precipitation (GNIP), using the Water Isotope System for Data Analysis, Visualization, and Electronic Retrieval (WISER) interface (IAEA/WMO, 2006).

A total of 29 rock samples were selected. Each rock sample collected was described and labelled in the field. Samples were crushed by a crushing machine to reduce the rock aggregate to $<0.063 \mu\text{m}$ particles. These samples were sieved to get the grain size fraction $<0.063 \mu\text{m}$. Sample powders were analyzed for their mineralogical composition using X-ray powder diffraction (XRD) technique using a Philips PW 1730 X-ray generator with Ni-filtered $\text{Cu-K}\alpha$, Fe-filtered $\text{Co-K}\alpha$, and non-filtered $\text{Fe-K}\alpha$ runs at 40 kV and 25 mA. All these analyses were performed at the Central Metallurgical R & D Institute (CMRDI), Cairo, Egypt.

The hydrochemical data was analyzed using a conventional statistical diagrams including Piper diagram (Hem, 1985). Hydrogeochemical data were analyzed and evaluated using NETPATH software (El-Kadi et al., 2011). This was done to quantify the set of reaction equations that controlled the water chemistry. The model is applied to reactions along flow of groundwater. The data used to solve the mass balance reaction model are a set of phases that are thought to be reacting along the flow path, and concentrations of the elements in the initial and final waters that correspond to the composition of the chosen phases.

5. Results

5.1. Isotope signature of groundwater

Stable isotope values for the precipitation in the study area are not available so a long-term measurements of precipitation at Adelaide Station (1962–1986) was obtained from the International Atomic Energy Agency's Global Network of Isotopes in Precipitation (GNIP), using the Water Isotope System for Data Analysis, Visualization, and Electronic Retrieval (WISER) interface (IAEA/WMO, 2006). The isotopic signature for precipitation has an average ratio of $\delta^{18}\text{O}$ and δD of -3.85% and -19.8% respectively. The difference in elevation, air temperature and source of water vapour between the Adelaide station and study area may result in different isotopic values in precipitation.

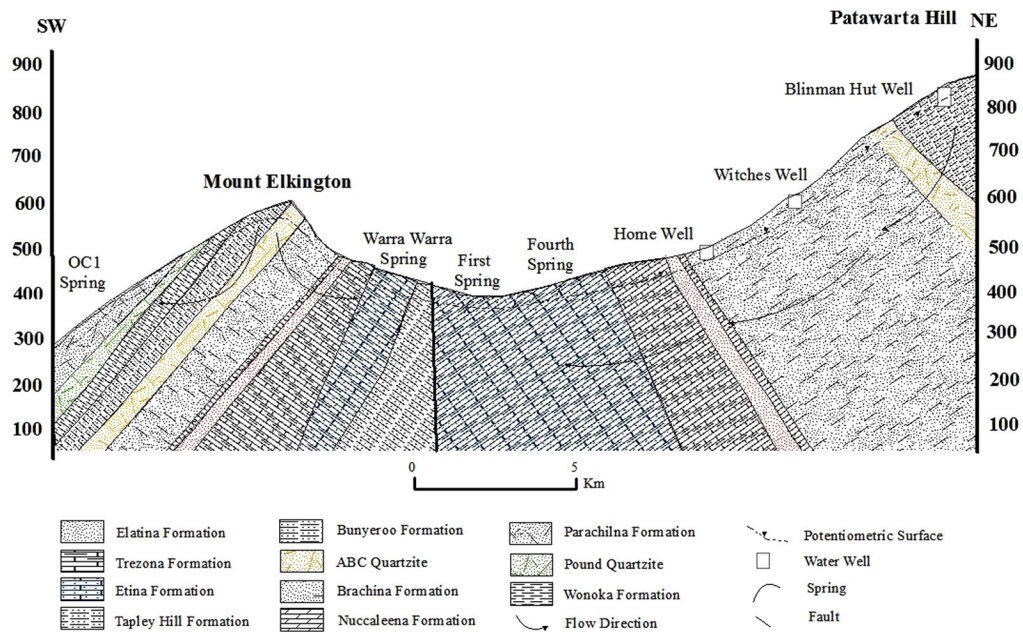


Fig. 4. Schematic cross section showing the main hydrogeologic units, location of the water points and direction of the water flow throughout the study area.

The results of the isotopic composition are tabulated in Table 1 and Fig. 5, all results are displayed in parts per thousand (‰). The stable isotope values for the groundwater ranges from -4.6% to -6.27% for $\delta^{18}\text{O}$, and $\delta^2\text{H}$ range is -38.2% to -30.4% . These values are closer to the local precipitation values and suggesting a local and good recharge in these areas. The isotopic depletion of samples like Third Spring and Breakneck Well relative to the Weighted Mean Precipitation of the Adelaide station (-4.6%), could be due to an altitude effect or to a climatic effect. To identify the altitude effect, it is essential to estimate quantitatively the recharge altitude of the depleted groundwater and confirm the relationship to the elevation of the aquifer outcrops in the recharge areas (Tarki et al., 2012; Dassi and Tarki, 2014). This can be done using the equation of Grabczak and Kotarba (1985), (Dassi and Tarki, 2014):

$$A = A_{\text{GNIP}} + (\delta^{18}\text{O}_{\text{GNIP}} + \delta^{18}\text{O}_{\text{CW}}/\text{AG})/100$$

Where A is the estimated recharge altitude (in m), A_{GNIP} is the altitude of the GNIP station (43 m a. m.s.l.), $\delta^{18}\text{O}_{\text{GNIP}}$ is the weighted mean of $\delta^{18}\text{O}$ in precipitation for the GNIP station (-4.6%), $\delta^{18}\text{O}_{\text{CW}}$ is the mean value of $\delta^{18}\text{O}$ in the depleted groundwater, and AG is the local altitudinal $\delta^{18}\text{O}$ gradient in precipitation ($\text{‰}/100\text{ m}$). By assuming an ^{18}O altitudinal gradient of 0.3% per 100 m with regard to the global variation range (Dassi and Tarki, 2014), no matching is found between the estimated altitudes of the potential recharge areas and the elevation of the aquifer recharge areas in the investigated area. Therefore, the altitude effect is not responsible for this depletion.

Climatic control is another physical effect that could result in depletion. It was identified as a complicated and varied physical process in precipitation (Liu et al., 2010). Several studies have correlated the mean isotopic compositions of precipitation and temperature (Dansgaard, 1964; Van der Straaten and Mook, 1983; Liu et al., 2010). Most of these studies indicate temperature effects of about $0.5\text{‰}/\text{°C}$ for $\delta^{18}\text{O}$ and about

Table 1
The hydrochemical analysis of the groundwater and precipitation rainfall (concentrations of ions in mg/l and EC in $\mu\text{s}/\text{cm}$).

| Well | EC | pH | Ca ²⁺ | Mg ²⁺ | Na ⁺ | K ⁺ | HCO ₃ ⁻ | SO ₄ ²⁻ | Cl ⁻ | TDS | $\delta^2\text{H}\%$ | $\delta^{18}\text{O}\%$ |
|------------------|--------|-----|------------------|------------------|-----------------|----------------|-------------------------------|-------------------------------|-----------------|--------|----------------------|-------------------------|
| Bore 170 | 1490.0 | 6.4 | 145.0 | 120.0 | 80.0 | 3.0 | 543.0 | 408.0 | 114.0 | 1413.0 | | |
| Blinman Well | 1714.0 | 7.1 | 112.0 | 114.0 | 182.0 | 4.5 | 643.0 | 216.0 | 285.0 | 1556.5 | | |
| Pendulum Well | 2160.0 | 7.2 | 103.0 | 177.0 | 264.0 | 6.4 | 559.0 | 360.0 | 521.0 | 1990.4 | | |
| Willigen Spring | 3640.0 | 7.1 | 171.0 | 130.0 | 508.0 | 5.0 | 545.0 | 424.0 | 860.0 | 2360.0 | -34.6 | -5.7 |
| Witches Well | 4470.0 | 6.7 | 188.0 | 221.0 | 532.0 | 4.5 | 662.0 | 378.0 | 1050.0 | 3035.5 | -36.9 | -6.1 |
| Home Well | 1930.0 | 6.3 | 234.0 | 248.0 | 404.0 | 3.5 | 628.0 | 636.0 | 851.0 | 3004.5 | -32.9 | -5.7 |
| Salt Bore | 8044.0 | 7.4 | 370.0 | 303.0 | 1450.0 | 10.8 | 558.0 | 1150.0 | 2480.0 | 6321.8 | -30.4 | -4.5 |
| Oratunga Bore | 1692.0 | 6.8 | 16.0 | 70.0 | 153.0 | 15.0 | 324.0 | 104.0 | 194.0 | 788.0 | | |
| Breakneck Well | 1791.0 | 7.3 | 92.0 | 85.0 | 160.0 | 5.0 | 469.0 | 102.0 | 320.0 | 1090.0 | -35.9 | -6.2 |
| Glass Gorge Well | 1692.0 | 6.8 | 117.0 | 65.0 | 166.0 | 4.0 | 470.0 | 96.0 | 301.0 | 1240.0 | -35.5 | -6.2 |
| Fourth Spring | 1262.0 | 6.0 | 121.0 | 49.6 | 155.0 | 2.7 | 421.0 | 89.1 | 310.0 | 1148.4 | | |
| Third Spring | 1904.0 | 7.0 | 119.0 | 53.0 | 171.0 | 3.0 | 358.0 | 104.0 | 367.0 | 1220.0 | -38.2 | -6.3 |
| First Spring | 1685.0 | 7.3 | 112.0 | 57.4 | 212.0 | 2.8 | 456.0 | 103.0 | 354.0 | 1297.2 | | |
| Warra Warra Well | 1648.0 | 7.2 | 76.0 | 54.0 | 146.0 | 2.0 | 353.0 | 86.0 | 245.0 | 922.0 | -33.1 | -5.5 |
| OC1 Spring | 1900.0 | 8.9 | 80.0 | 59.0 | 211.0 | 5.0 | 305.0 | 169.0 | 373.0 | 1150.0 | | |
| Rainwater | | | 3.32 | 1.27 | 9.54 | 0.6 | 9.67 | 3.63 | 18.06 | | -20.2 | -4.2 |

*Rainfall chemistry from (Crosbie et al., 2012).

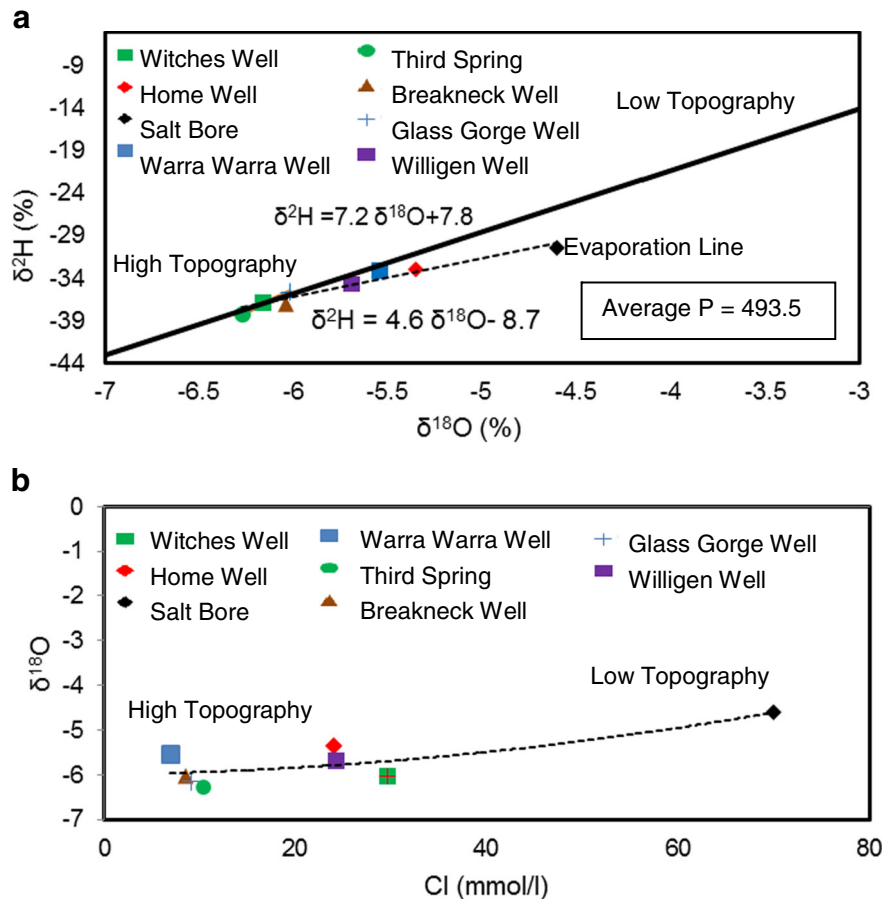


Fig. 5. Relationship between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ compositions of the groundwater samples collected from the study area and the Local Meteoric Line of Adelaide (a) $\delta^{18}\text{O}$ and chloride plot show the evolution of groundwater within the study area (b).

5‰/°C for $\delta^2\text{H}$. Within the study area, the variation in climate does not exist. Thus, the position of these samples is clearly close to the LMWL, which indicates that the air mass evolution was that of the present day, with little evaporation and evolution from its source (Edmunds et al., 2003). Stable isotope content of water in semi-arid regions is likely to be controlled more by precipitation amount and intensity than those in temperate regions, where temperature effects dominate (Clark and Fritz, 1997; Liu et al., 2010). In the Oratunga Area, the groundwater system recharge depends mainly on rainwater infiltration. Evaporation and infiltration are the main factors impacting the dynamics and recharge of groundwater in the arid environment. These are more related to other parameters such as soil properties, hydraulic conductivity and vegetation cover.

In this area, samples from Home Well, Salt Bore and Witches Well exhibit the more enriched $\delta^{18}\text{O}$ and $\delta^2\text{H}$ contents. The enrichment could be attributed either to evaporation of meteoric water during recharge, or to water–rock interactions following recharge (Allison et al., 1985). The $\delta^{18}\text{O}$ and chloride relationship indicates that lighter isotopic values are associated with lower chloride concentrations and that heavier values are associated with the higher chloride concentrations (Fig. 5). The chloride is then considered conservative in the groundwater and the only process that may change its concentration is evapotranspiration during recharge, and/or mixing with groundwater of different chloride composition. It can be used to estimate the recharge using chloride mass balance.

Assuming a steady-state condition, the balance can be represented mathematically as:

$$R = \text{Clp} P / \text{Clg}$$

Where R is the average recharge rate (mm/yr.), Clp is the average Cl concentration in atmospheric precipitation (mg/L), Clg is the groundwater Cl concentration in (mg/L), and P is the mean annual rainfall in mm/year (Bazuhaire and Wood, 1996). The recharge value was estimated using the weighted mean chloride concentration in rainwater (8.76 mg/L) (Crosbie et al., 2012), the long-term mean annual rainfall in the study area (290 mm) and the average chloride concentrations in groundwater (553 mg/L). The recharge ranged from 1.02 to 22 mm/yr (Unpublished work by the author). The highest estimated recharge occurred in the high topographic areas while the lowest values were estimated in low areas regions. The most enriched $\delta^2\text{H}$ and $\delta^{18}\text{O}$ groundwater signatures are found in areas with lower recharge rates (Salt Bore), in the central and western areas, while the depleted isotopic signatures of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ groundwater are found where recharge rates are relatively higher.

5.2. Digital elevation analysis

The SRTM was used to delineate the basin area under analysis. The Oratunga Area covered by the different altitude ranges (Fig. 6). The presence of these significant variations makes using 30 m resolution SRTM images necessary. The elevation ranges from 200 m to

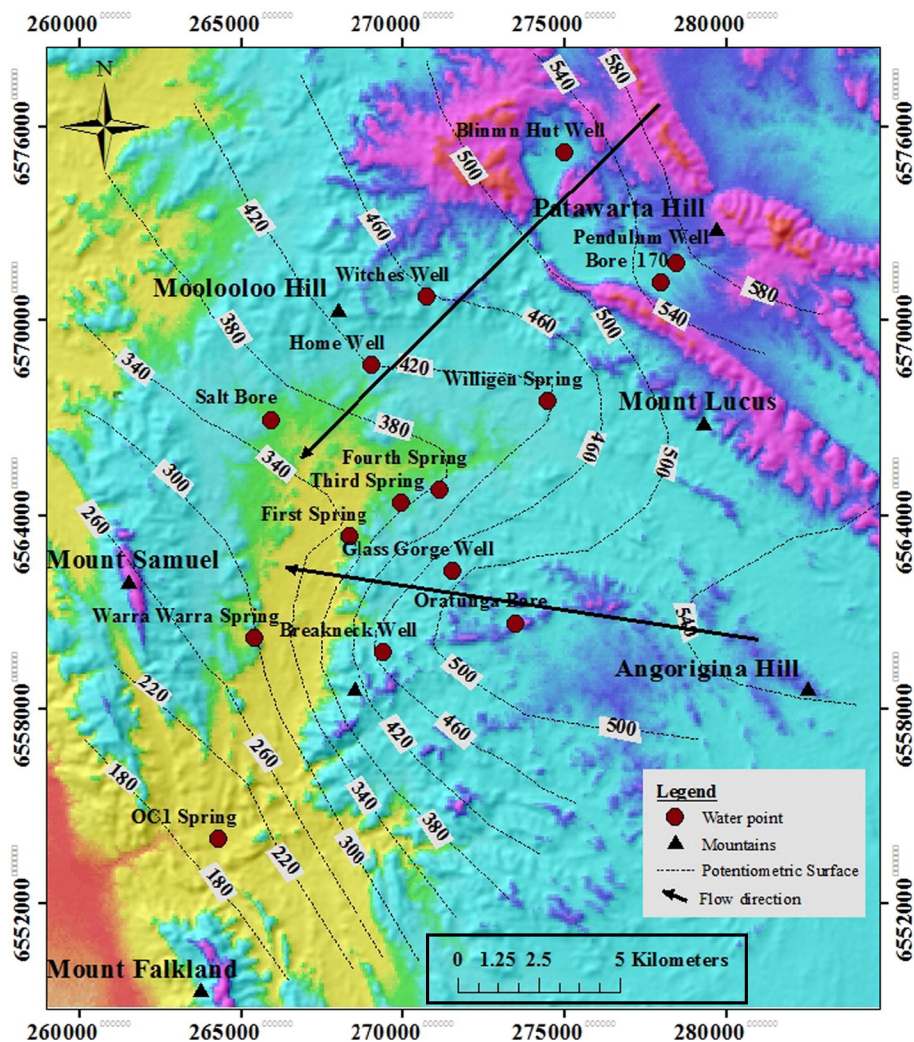


Fig. 6. Sampling water points, contours and main groundwater flow directions throughout the Oratunga Area.

>800 m. The highest elevation of 850 m is located on the Patawarta Hill range in the north eastern part of the study area. It constitutes the highlands and the prominent water divide for the basin. A similar range of elevation is in the southern and northern parts of the area where the Mount. Elkington, Mount. Lucus and Anorigina Hill are present. The lowland area is the most extensive, and it covers the central and western parts of the study area. Its elevation ranges from 200 m to 500 m. (See Fig. 6)

Data on potentiometric heads indicate that the potentiometric surface resembles that of the land surface elevation. In the study area, the highest values in the northeastern part where the surface topography is greatest, and lowest in the central and south-western part of the catchment, where the surface topography is low. Groundwater flow is dictated by this descent in the potentiometric head elevation. Hence, groundwater flow throughout the majority of the Oratunga Area is in central and western directions.

In order to support the flow regime, the general trend of increasing ionic concentration along the flow path can be used. The Ca^{2+} distribution seems to follow the TDS distribution with low concentrations observed from in the far northeast and southeast areas increasing in the direction of water flow. Also, the ionic ratios of water samples were used to confirm the groundwater flow directions. The ratios show an increase from the regions of high

topography towards the centre of the study area and regions of low topography which clearly shows the direction of flow of groundwater (Fig. 7).

In addition, the saturation indices for carbonate, silicate and evaporite minerals are shown in Table 2. The calculations indicate that indices of carbonate minerals have both negative and positive values, indicating the occurrence of carbonate minerals in the solution. The saturation indices of gypsum and anhydrite reflect high negative values, indicating sub-saturation and potential for dissolution of these minerals. In general, the groundwater is saturated with respect to quartz and undersaturated with respect to amorphous silica suggesting that silicate weathering possibly controls the groundwater composition. (Table 2)

The saturation indices calculations indicate that they progress as the increase in water salinity of the flowing water towards the central and western areas (Fig. 8). The graphs indicate a relationship between the indices of water saturation towards the calcite as a function of $\text{Ca}^{2+} + \text{HCO}_3^-$, and gypsum as a function of $\text{Ca}^{2+} + \text{SO}_4^{2-}$ respectively. The saturation state indicates the evolution along flow, precipitation is expected for calcite and dissolution is expected for dolomite and gypsum (Appelo and Postma, 2005). However, the semi arid climate and the result of evaporation are another sources for these ions into the groundwater (Srinivasamoorthy et al., 2008).

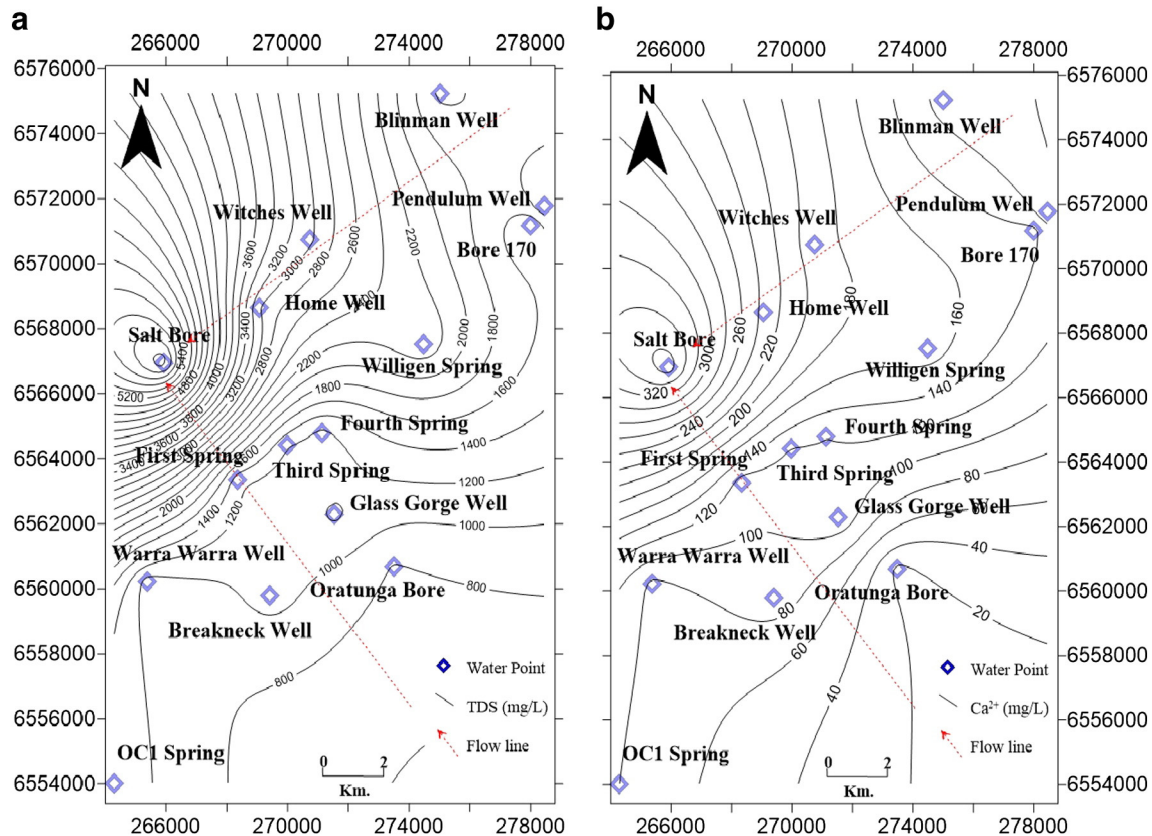


Fig. 7. Spatial distribution of (a) TDS and (b) Ca showing the increase of concentrations from the high areas to the lower areas within the study area.

5.3. Hydrochemical classification

Piper diagram is a commonly used tool to show the linear trends of cations and anions along groundwater flow (Hem, 1985). The chemical analyses of the wells and springs were plotted on Piper diagrams for hydrochemical classification (Fig. 9). Distribution of the groundwater samples in the Piper diagram shows alteration from magnesium calcium bicarbonate or no dominant water type in the high topographic areas to the Na–Cl type that predominates under lower topographic areas. This is a common phenomenon in semi-arid to arid groundwater aquifers (Herczeg and Edmunds, 2000). Hence, the groundwater can be divided into two groups based on their chemical compositions: Dilute calcium and sodium-bicarbonate type water (Group I) with relatively low concentrations of chloride and sulfate occurs in the recharge areas

(Bore170, Blinman Well, Glass Gorge Well and Breakneck Well). The Group II water is made up of sodium–chloride water type. This type is characterized by low concentration of HCO₃⁻ and relatively higher concentration of Cl⁻ which are mainly distributed among the fine sediments, occurs in the low topographic and discharge area.

Durov plot is another composite plot consisting of 2 ternary diagrams where the cations of interest are plotted against the anions of interest; sides form a binary plot of total cation vs. total anion concentration. The diagram gives more insight to the hydrochemical facies by identifying chemical processes and by classifying groundwater types accordingly (Chadha, 1999). In this study, the Durov diagram is compared with the Piper diagram to understand the geochemical processes and to follow the groundwater evolution in the study area. Water samples of the Oratunga Area were plotted into the Durov

Table 2

The saturation indices of the groundwater with respect to different minerals. Negative values indicate under saturation and positive indicate saturation.

| | Calcite | Dolomite | Gypsum | Anhydrite | Quartz | Chalcedony | SiO ₂ | pCO ₂ |
|------------------|---------|----------|--------|-----------|--------|------------|------------------|------------------|
| Bore 170 | -0.4 | -0.6 | -1.0 | -1.2 | 0.6 | 0.2 | -0.6 | -0.7 |
| Blinman Well | 0.3 | 1.1 | -1.4 | -1.6 | 0.4 | 0.0 | -0.9 | -1.3 |
| Pendulum Well | 0.2 | 0.9 | -1.3 | -1.5 | | | | -1.5 |
| Willigen Spring | 0.3 | 0.7 | -1.0 | -1.3 | 0.5 | 0.1 | -0.8 | -1.5 |
| Witches Well | 0.0 | 0.4 | -1.1 | -1.3 | 0.6 | 0.2 | -0.6 | -0.9 |
| Home Well | -0.3 | -0.3 | -0.8 | -1.0 | | | | -0.6 |
| Salt Bore | 0.8 | 1.8 | -0.6 | -0.8 | 0.4 | 0.0 | -0.8 | -1.7 |
| Oratunga Bore | -1.2 | -1.5 | -2.3 | -2.6 | 0.3 | -0.1 | -1.0 | -1.4 |
| Breakneck Well | 0.2 | 0.7 | -1.7 | -1.9 | 0.4 | -0.1 | -1.0 | -1.7 |
| Glass Gorge | -0.2 | -0.4 | -1.6 | -1.8 | 0.4 | 0.0 | -0.9 | -1.2 |
| Fourth Spring | -1.0 | -2.2 | -1.6 | -1.8 | | | | -0.5 |
| Third Spring | -0.1 | -0.2 | -1.6 | -1.8 | 0.4 | -0.1 | -0.9 | -1.5 |
| First Spring | -1.7 | -3.5 | -1.5 | -1.8 | 0.8 | 0.3 | -0.6 | -3.6 |
| Warra Warra Well | 0.1 | 0.5 | -1.8 | -2.0 | 0.2 | -0.2 | -1.0 | -1.7 |
| OC1 Spring | 1.5 | 3.3 | -1.6 | -1.8 | 0.1 | -0.3 | -1.2 | -3.6 |

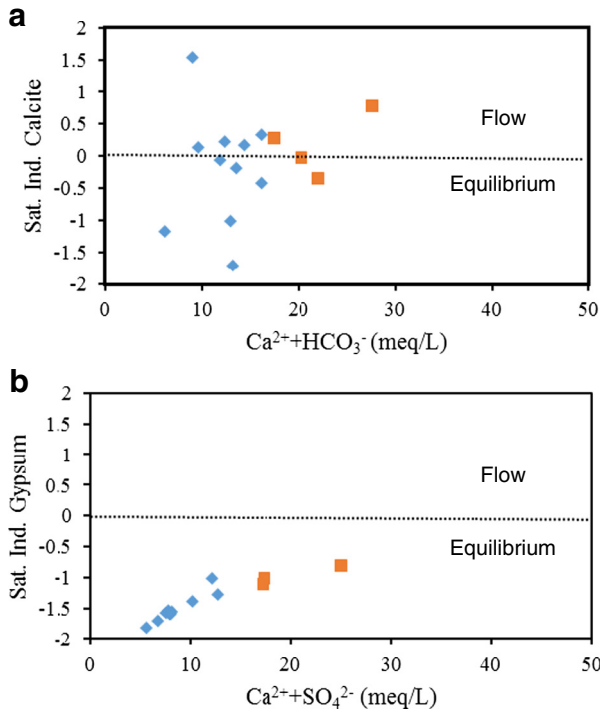


Fig. 8. Scatter plots of $\text{Ca}^{2+} + \text{HCO}_3^-$ and $\text{Ca}^{2+} + \text{SO}_4^{2-}$ versus saturation indices of calcite (a) and gypsum (b) showing the evolution of groundwater towards the low areas. The equilibrium line is indicated for each plot.

diagram for hydrogeochemical process analysis. Samples from the high topographic areas are classified as HCO_3^- or no dominant water types and located in dissolution field. They coincide with zone 4 in the Piper

diagram (Fig. 10). Groundwater seems to be affected by the composition and solubility of rock materials in the soil or bedrock and loss or gain of constituents as water percolates through clay layers.

Samples collected from the lower topographic and discharge areas are classified as Na–Cl water type and are located in the ion exchange field, these samples represents endpoint water (Zaporozec, 1972). It is consistent with samples in zone 2 in the Piper diagram. The arrows on this diagram show the groundwater evolution in the Oratunga Area. Thus, the diagram plot revealed that the groundwater is in the final stage of evolution, represented by a Na–Cl water type. Groundwater evolution along flow seems to be significantly affected by same identified chemical processes.

5.4. Mineralogical and geochemistry of rocks

In an attempt to understand the controlling hydrogeochemical processes in the groundwater of the area, samples from four water bearing units (Tapley Hill, Etina, Brachina and Bunyeroo formations) and were collected and studied to define their mineralogical and chemical composition using X-ray diffraction (XRD). An analysis of the majority of rock samples showed that the occurrence of quartz and albite, clay and feldspar and the predominant carbonates, calcite and dolomite (Fig. 11).

5.5. Ionic ratios

Generally, the chemical composition of groundwater is mainly dependent on the geochemical processes along the flow paths within the groundwater system. In the Oratunga Area, it is assumed to be influenced by many chemical reactions which can be used to infer the sources of the different ions in the groundwater. Plotting the different species against each other can reflect the mechanisms controlling the water chemistry (Fig. 12).

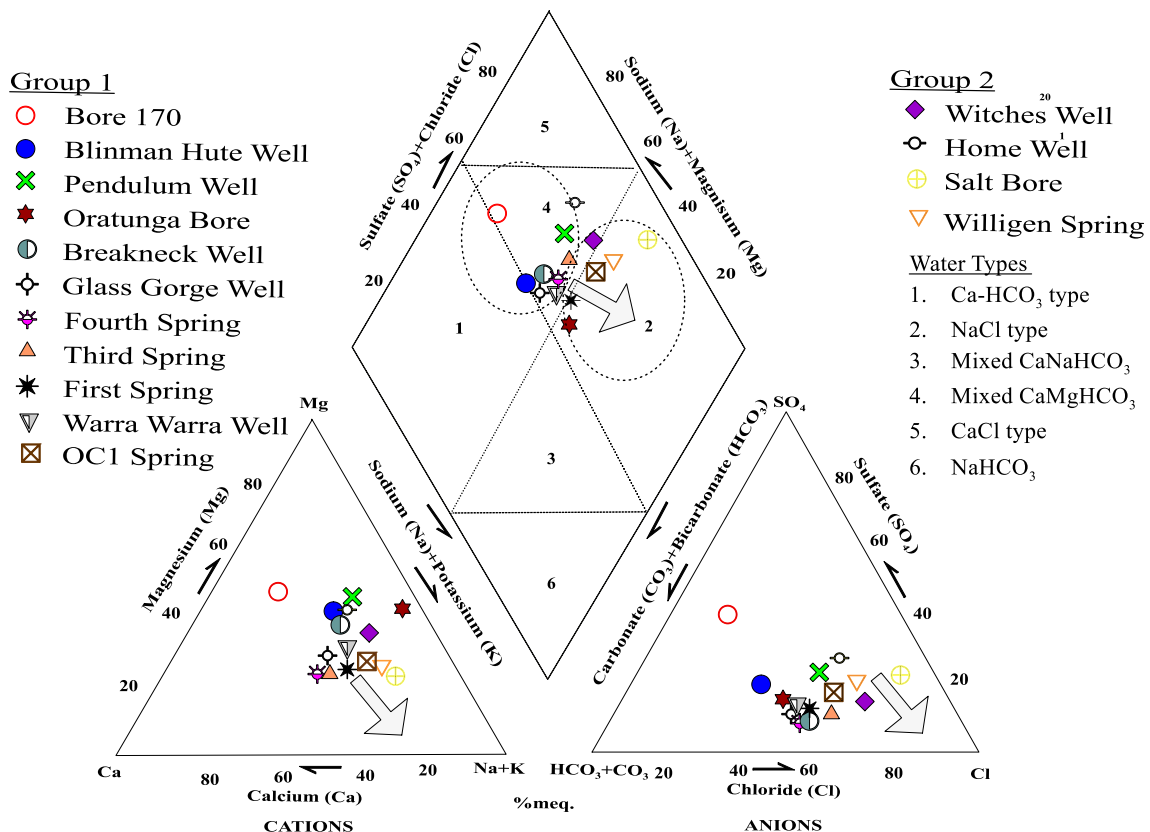


Fig. 9. Piper diagram showing the water types and the evolution of groundwater the mixed types (Group 1) towards the Na–Cl type (Group 2).

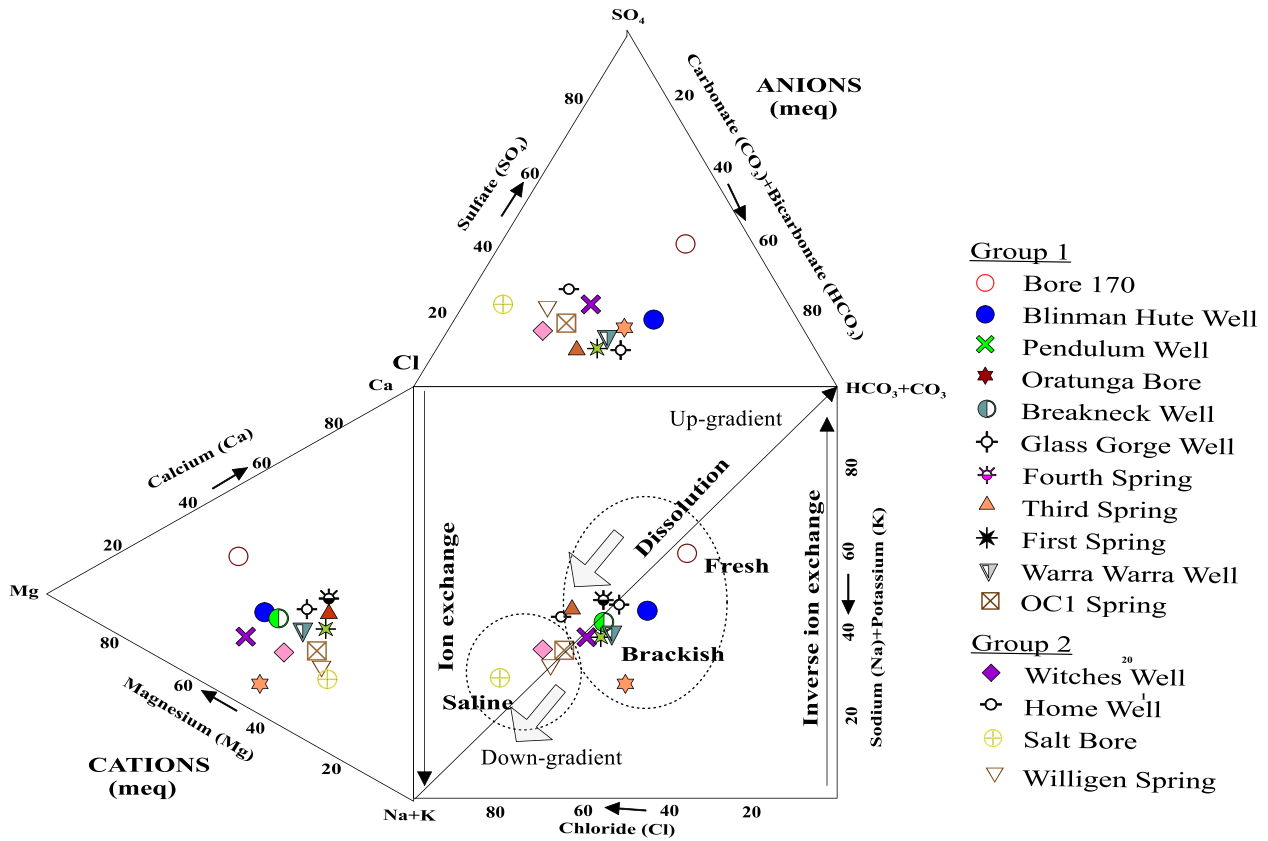


Fig. 10. The Durov diagrams reflecting the dominance of dissolution and dilute water in the high topographic areas and ion exchange in the low topographic areas.

The geochemical evolution results from the interaction of water that contains oxygen and carbon dioxide with soils and rocks. Thereby, the higher the concentration of gases in the water, the more effective the groundwater reacts. The studied water along the proposed flow trends

characterize by high CO₂ content (0.125, 0.25 and 0.018 atm.). The mean CO₂ pressures show levels of 10–3.5 atm. And 10–1.5–10–2.5 atm. For atmospheric and soil, respectively conditions (Appelo and Postma, 2005). The high characteristics of the water along the

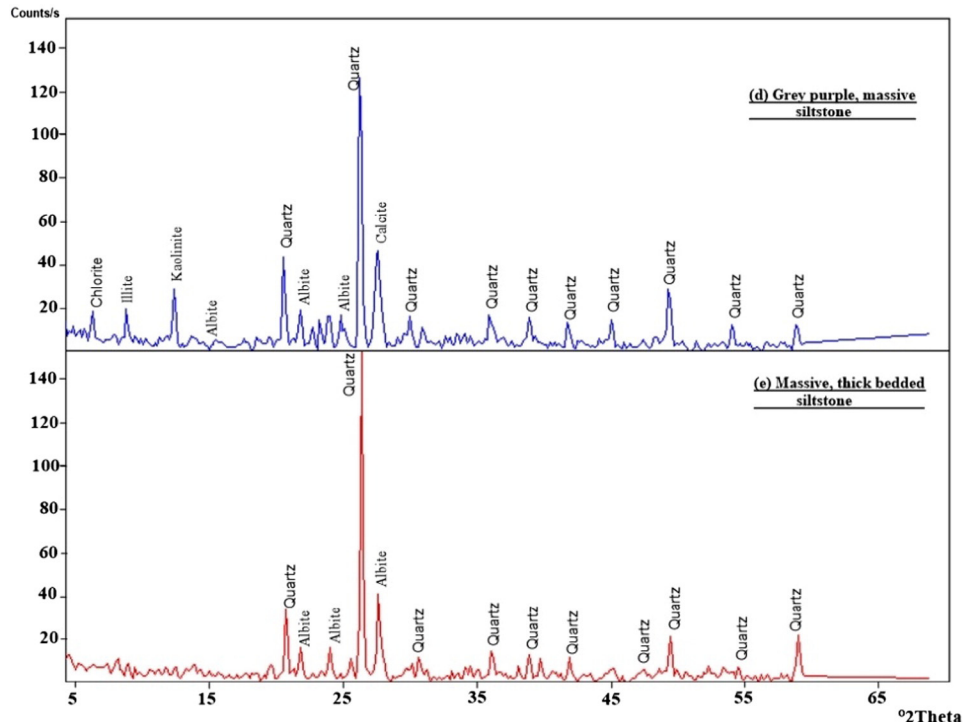


Fig. 11. Example of the XRD patterns of the studied samples from the Brachina Formation. The main phases detected by X-ray diffraction were quartz, albite, illite and chlorite.

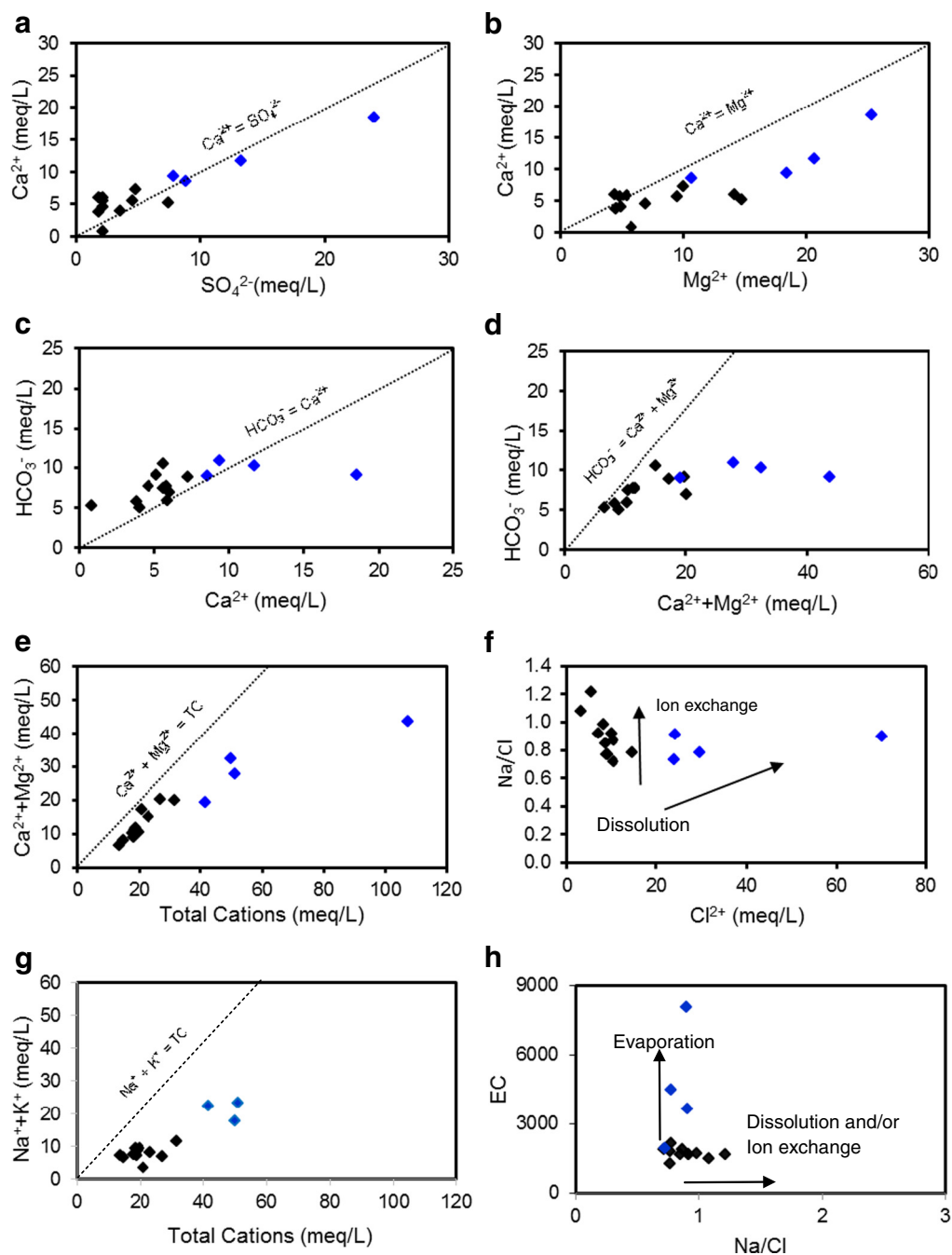


Fig. 12. Relationships between various ions in groundwater (black blocks for group 1 from high topographic areas and blue for group 2 from low topographic areas).

evolutionary trend suggest that reactions take place largely under partially open or open-system. CO_2 may be derived from a variety of sources, including release of CO_2 by oxidation of organic matter and the interaction of water with carbonates.

In the study area, calcareous rocks are exposed and in contact with groundwater. The results from the XRD of various rocks revealed that calcite and dolomite are common minerals in the studied rocks. Therefore, carbonate dissolution is likely to be an active process determining the chemical evolution of groundwater. The mechanism of this dissolution and/or precipitation is mainly controlled by the behaviour of CO_2 (Appelo and Postma, 2005). The carbonate dissolution is also supported by plotting of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ versus total cations (Fig. 12e) samples lying under the 1:1 trend reflect a decreased contribution of Ca^{2+} and Mg^{2+} suggesting a common source for these ions (Rajmohan and

Elango, 2004). This is most likely supplied by the weathering of various minerals such as dolomite and calcite (Freeze and Cherry, 1979).

If the dissolution of calcite is a dominant process controlling the chemistry of natural groundwater, then Ca^{2+} and HCO_3^- will correlate to a 1:1 line (Fig. 12c). The relationship between Ca^{2+} and HCO_3^- shows an excess of HCO_3^- relative to Ca^{2+} for the higher topographic points. This suggests that calcite dissolution is common in these areas. In the topographically low areas, Ca^{2+} concentration may be low due to calcite precipitation and cation exchange. Dissolution of dolomite may also provide Mg^{2+} for the solution. When the Mg^{2+} and Ca^{2+} are plotted against HCO_3^- (Fig. 12d) then the majority of the data are located along the 1:1 line which confirms that dolomite dissolution is a significant chemical process. The correlation between Ca^{2+} and Mg^{2+} shown in Fig. 12b, thus, at low concentrations in higher topographic

areas, the Ca^{2+} and Mg^{2+} concentration plot close to the 1:1 ratio, with increasing in concentration, Mg^{2+} become more than Ca^{2+} . This may be due to the precipitation of calcite over dolomite. Furthermore, in Ca^{2+} versus SO_4^{2-} plot (Fig. 12a), the distribution of water samples are mostly above 1:1 line indicating the dominance of carbonate weathering. These results are also consistent with the calculated saturation indices. The SI of calcite and dolomite for most samples in the higher areas are above saturation with respect to calcite which also does recommend that dissolution is a significant hydrogeochemical process. The same is evident for the SI of dolomite distribution with a difference in high values of this distribution towards the discharge and lower areas. This suggests that the mineralization of groundwater is controlled by the weathering of carbonate rocks.

The results from the XRD of various rocks shown that silicate minerals are dominant in the studied rocks. So, silicate weathering is another key geochemical processes controlling the major ions chemistry of the groundwater, especially in fractured rock aquifers (Rajmohan and Elango, 2004). Silicate weathering can be supposed by estimating the ratio between $\text{Na}^+ + \text{K}^+$ and total cations (Fig. 12g). The relationship between $\text{Na}^+ + \text{K}^+$ and total cations of the studied samples indicate that all samples are plotted where the $\text{Na}^+ + \text{K}^+ = 0.5$ total cations line (Fig. 12g). The relationship shows the contribution of silicate weathering in the geochemical processes, which adds mainly sodium ions to the groundwater (Stallard and Edmond, 1983). Feldspars are more susceptible for weathering and alteration than quartz in silicate rocks. Weathering of soda Feldspar (Albite) and Potash Feldspars (Microcline) may contribute Na^+ ions to groundwater.

In the Oratunga Area; the presence of clay rich rocks may permit the groundwater to be well-maintained for a long time causing the ion exchange to occur (Faust and Aly, 1981). Plotting of Na/Cl versus Cl suggest that the concentration of Na in the groundwater is dependent on both ion-exchange and dissolution processes (Fig. 12f). Therefore, ion exchange and dissolution of feldspars are likely to be another source of ions (Herczeg et al., 1991). The presence of fractures, faults and intercalated shale beds in the study area may contribute the ion exchange process (Abdalla and Scheytt, 2012). However, in arid climatic conditions, evaporation could cause an increase in the concentrations of all species in the water. If the evaporation process is dominant, and no mineral species are precipitated (Jankowski and Acworth, 1997). To identify the evaporation effect, a plot of Na/Cl versus EC could be used (Fig. 12h). The Na/Cl versus EC shows that there is one horizontal trend which indicate dominance of evaporation and the other trend indicates that dissolution or ion exchange are common processes.

5.6. The hydrochemical modelling

On the basis of the analysis of the rock samples, saturation indices, ionic ratios and chemical trends along the observed flow paths, the observed reaction hypotheses were tested using a mass-balance geochemical model. Two distinct hydrochemical processes were considered in determining the chemical evolution of the groundwater. These were reactions of meteoric water as it infiltrates through the unsaturated zone to the groundwater, and 2) reactions of groundwater as it moves from topographically high area (recharge area) down gradient to topographically low area (discharge area). The limitations imposed by mineral saturation and mass balance are then applied to constrain the set of reactions into a model that explains the chemical evolution of the groundwater along the flow path, and describes the similar patterns of changing groundwater composition observed along other flow paths. Calcite and dolomite are thermodynamically preferred to dissolve and contribute calcium, magnesium and bicarbonate ions into the groundwater system. Carbon dioxide is included as a source of carbon in addition to calcite. The presence of clays indicates the potential for cation exchange reactions and/or silicate weathering.

According to hydrochemical trends, one flow path was chosen to support the geochemical evolution of groundwater in this area. Three

Table 3

The results of the geochemical modelling (in mg/L) for the selected water points. Negative values indicate precipitation and positive indicate dissolution.

| Phases | Rainfall-Witches Well | Witches Well –Home Well | Home Well –Salt Bore |
|----------------|-----------------------|-------------------------|----------------------|
| Calcite | – 1.6 | – 6.6 | – 4.2 |
| Dolomite | 1.1 | 3.9 | – 6.0 |
| Exchange | – 0.5 | – 0.8 | 2.2 |
| Gypsum | 0.5 | 4.6 | 9.6 |
| Na-Cl | 3.6 | 1.0 | – 1.6 |
| SiO_2 | 0.1 | – 0.4 | 0.1 |
| CO_2 | 1.1 | 8.3 | – 4.2 |

water points assumed to study the groundwater evolution according the hydraulic heads, TDS and ionic ratios. The evolutionary trend of the groundwater continues from a Na-Mg-Cl- HCO_3 - SO_4 in the assumed recharge area at Witches Well (TDS = 3035 mg/L) to intermediate Mg-Na-Ca-Cl- SO_4 Home Well (TDS = 3004) and finally a more concentrated Na-Mg-Cl- SO_4 water at Salt Bore (TDS = 6321 mg/L). The NETPATH model results provided as many possible models based on different constraints and phases used (Table 3).

The evolution of the Na-Cl precipitation water to Na-Mg-Cl- HCO_3 (Witches Well) involves the dissolution of both CO_2 in soil zone and weathering of silicates and carbonates. Thus precipitation of calcite and dissolution of dolomite result in release of Mg^{2+} and HCO_3^- ions into solution while dissolution of silicates and/or ion exchange increases the Na ion with a subsequent formation of kaolinite and other clay minerals. Dissolution of atmospheric salts may also be the source for chloride increase.

The low pH values and dominance of Na^+ and Cl^- ions are characteristic of Na-Mg-Cl- HCO_3 water type. It is probably indicated the short residence times within the groundwater flow system than other types. It represent recent infiltration of acidic recharge waters through the unsaturated zone to the upper part of the water bearing rocks, where carbonate is present or has been largely dissolved by weathering. Then the groundwater evolves from Na-Mg-Cl- HCO_3 water (Witches Well) to Mg-Na-Ca-Cl- SO_4 - HCO_3 (Home Well) can occur as a result of many processes including dissolution and/or precipitation of carbonates and silicates which released additional Mg^{2+} , Na^+ and HCO_3^- into solution. There is a general increase in concentration of Mg^{2+} and Ca^{2+} along the flow path.

Moreover, it is evident that there is an overall increase in the SO_4^{2-} . Although the results show dissolution of gypsum as a significant source for sulfate, in the study area, dissolution of pyrite seems to be a possible source of this ion. The occurrence of pyrite in the rocks and oxygen might produce sulfate and hydrogen ions as well as iron hydroxide precipitate. Therefore the oxidation reaction is considered a common reaction and the main contributor to sulfur in the groundwater. Increasing CO_2 gas is also noticed and confirmed the open system which required addition and increasing of CO_2 . The Salt Bore in the northwest area has quite different composition from the low salinity water in the rest of the area. Na-Mg-Cl- SO_4 water is distinguished with high saline water. Thus, Na-Cl water can be described as the end result of a number of geochemical processes (Freeze and Cherry, 1979).

6. Discussion

In the Oratunga Area, the lithological and topographic variations can change the chemical composition, flow and distribution of recharge and discharge areas. As observed, the chemical results show distinct hydrochemical features across the Oratunga Area. For most of the chemical parameters measured there were two distinct areas: (1) an area of high parameters was found within the low topographic features in the central and western areas. (2) Another area with low parameters was found on the high topographic areas along the marginal areas in the far north and the south.

The water-type distribution in the Piper and Duorv diagrams which was assigned as recharge, evolution and discharge areas according to their topographic location, agree with the evolution of groundwater chemistry. Dilute calcium and sodium-bicarbonate type water with relatively low concentrations of chloride and sulfate occurs in the recharge areas. The low compositions of these constituents in the rain samples and high composition in groundwater samples may be due to rapid recharge through times which result in less interaction of the water with the weathered sediments exposed in these areas. The magnesium-calcium bicarbonate waters may result from the dissolution of carbonate minerals or cation exchange processes with surrounding clays and clay minerals. The moderately higher TDS and the dominance of Na—Cl type for groundwater and water from springs may be due to a longer time of contact with the dominant fine sediments and/or a moderate interaction with the atmosphere and evaporation which leads to concentration of salts in groundwater (Herczeg and Edmunds, 2000). In the flow path model, there is considerable agreement in the model output and its compatibility with the observed chemical and the calculated mass transfer of the selected minerals phases. The obtained models represent the evolutionary trends in three steps: from rainfall to recharge water, from recharge water to intermediate evolved (transit area) water, and from intermediate evolved water to evolved water (discharge area).

The evolutionary trends show enrichments in Na^+ and Cl^- concentration which is possibly due to long-term water rock interaction; evaporative concentration; the dissolution of halite and mixing of connate water and meteoric water (Rogers, 1989; Kresic, 2006). As sodium feldspar (Albite) was identified in the XRD data, dissolution of sodium feldspar is a possible mechanism providing excess Na^+ . The albite dissolution consumes hydrogen ions of carbonic acid and produces bicarbonate ions, which increase the alkalinity and pH of the groundwater (Freeze and Cherry, 1979). For the groundwater along the evolutionary trend, the increase in Na^+ and a decrease in HCO_3^- are obvious. The decrease in HCO_3^- in water and the low content of Na_2O support the occurrence of different reactions than the silicate hydrolysis. Therefore, the effects of feldspar dissolution are not likely to produce significant geochemical changes. Groundwater can also add Na^+ if it flows across highly soluble minerals. Although the currently under-saturated state with respect to halite and Na/Cl ratios ($\text{Na/Cl} < 1$) clearly supports that the dissolution of halite is unlikely the appropriate conditions existed for the addition of Na^+ ion. It is therefore that the Na excess water did not form as a result of evaporites dissolution as the groundwater migrated through the Brachina Formation.

Another possible mechanism is evaporative concentration. The $\delta^{18}\text{O}$ and δD data suggest that water of Witches Well and Home Well are more depleted and diluted water while that Salt Bore is enriched and saline. The recharge values confirm the evaporative effects in the unsaturated zone which seem to be more effective when the recharge rate is less than about 1 cm/year (Fontes et al., 1986). Areas of high recharge in the north eastern and southern edges have been less influenced by these effects and areas in the southern areas are more subject to evaporative effects. Dilution of groundwater may also occur, especially during the rainy seasons in the unsaturated zone, a phenomenon that has been observed in a wide range of environments (Mathieu and Bariac, 1996).

Therefore, evaporation as a major process was considered to be influenced the water composition in the evolutionary trend. The meteoric origin is also supported by the values of Na/Cl ratios for the groundwater. The value of this ratio for seawater is 0.85, Na/Cl ratios of Witches and Home wells are closest to the standard seawater value and this indicate the meteoric origin of the groundwater, while for the Salt Bore, the value is slightly more than the standard seawater values suggesting evolution of water. The high Na^+ groundwater may also explained as a mixing of meteoric water with existing saline water which results removing the original water. A marine source for the groundwater is suggested since the area is outcropped mainly by marine sediments (Preiss, 1987). The occurrence of saline water is probably resulted in the

adsorption of sodium on the clays in the shales and siltstones. As water contain calcium and bicarbonate, these were slowly flushed the saline water from the rocks, the adsorption of the dissolved calcium and magnesium on the clays occurred releasing sodium to solution. The decrease in calcium concentration permits more dissolution and additional calcium and bicarbonate to the water. The added calcium then existed for more exchange with sodium.

Further, if chloride is not affected by ion exchange, the Na/Cl ratio can be a potential tracer to understand the washing out the marine sediments. The Na/Cl ratios increase from the Witches and Home wells towards the Salt Bore indicating that the recharge water replaces the saline water or flushing the marine sediments. The presence of clay rich lithologies in this area permits the groundwater to be retained for a long time causing the ion exchange to occur (Faust and Aly, 1981). Clay minerals and albite were detected by the XRD analysis in some of the rocks. These may dissolve under acidic conditions to yield sodium and silica ions (Herczeg et al., 1991).

As indicated that with residence time (distance of transport) of groundwater increases, calcium and magnesium increase while bicarbonate shows a noticeable decrease. The groundwater composition has changed significantly by interaction with carbonate minerals. It is possible that that change in water chemistry resulting from precipitation/dissolution of carbonate minerals. Most of soils and rocks in the Oratunga Area contain amounts of carbonate minerals. During infiltration of rainfall, the dissolution of carbonate minerals adds calcium, magnesium and bicarbonate ions and increases the pH of groundwater. But also dissolution of these carbonates in the presence of carbonic acid produced from the mineral itself should add to the bicarbonate remaining from the disassociation of carbonic acid and this is not evident. This decreasing of bicarbonate is attributed to availability of CO_2 . Water percolating through the soil becomes enriched in CO_2 and then dissolves carbonate. As this water reacts with calcite the CO_2 gets consumed, and, there is no additional source of CO_2 the water become saturated with respect to calcite and not be able to dissolve the rock. The Ca/Mg ratios for the groundwater samples are more than that of seawater which reflect enrichment of Ca by dissolution of carbonate minerals in the rock matrix or in the fracture zones. However, the increase in ratios between water in the Witches and Home wells to the higher Salt bore and the close to unity is likely indicating that either dolomite dissolution or Mg enrichment along the movement of groundwater is the common process. A change along groundwater flow in the Oratunga Area appears to be dominated by the dissolution/precipitation of minerals in the soils and rocks matrix. The groundwater contains sodium, calcium and magnesium balanced with chloride, sulfate and bicarbonate. As this groundwater flow down the hydraulic gradient they are modified by these processes.

Other naturally occurring constituent of interest along the evolutionary trend is sulfate. The increase in sulfate concentration can be attributed to dissolution of sulfate minerals and/or oxidation of sulfide bearing minerals. Soil of the Oratunga Area may include gypsum, a very soluble mineral. Recharge passing through soil and underlying rocks with soluble gypsum can substantially increase the calcium and sulfate content. In that case calcium-sulfate waters result and this water type is not identified along the flow path. Also, the saturation indices of both anhydrite and gypsum are very low; sulfate dissolution does not seem very likely in much of the study area.

The Ca/SO_4 ratio is also taken as a guide for detecting any excess of sulfate. In groundwater associated with sulfate mineral dissolution, the Ca/SO_4 ratios should be gradually increased along the evolutionary trend from Witches Well to the Salt Bore and this is not evident. The observed ratios indicate other sources than the soluble evaporite minerals. The fine grained rocks in the Oratunga Area contain the mineral pyrite (FeS_2). The pyrite weathers to produce dissolved iron and sulfate. The iron can then oxidize and precipitate as iron oxides which produce the red coloration commonly occurring in different rock units. The solution from pyrite weathering is acidic and dissolves additional calcite in a

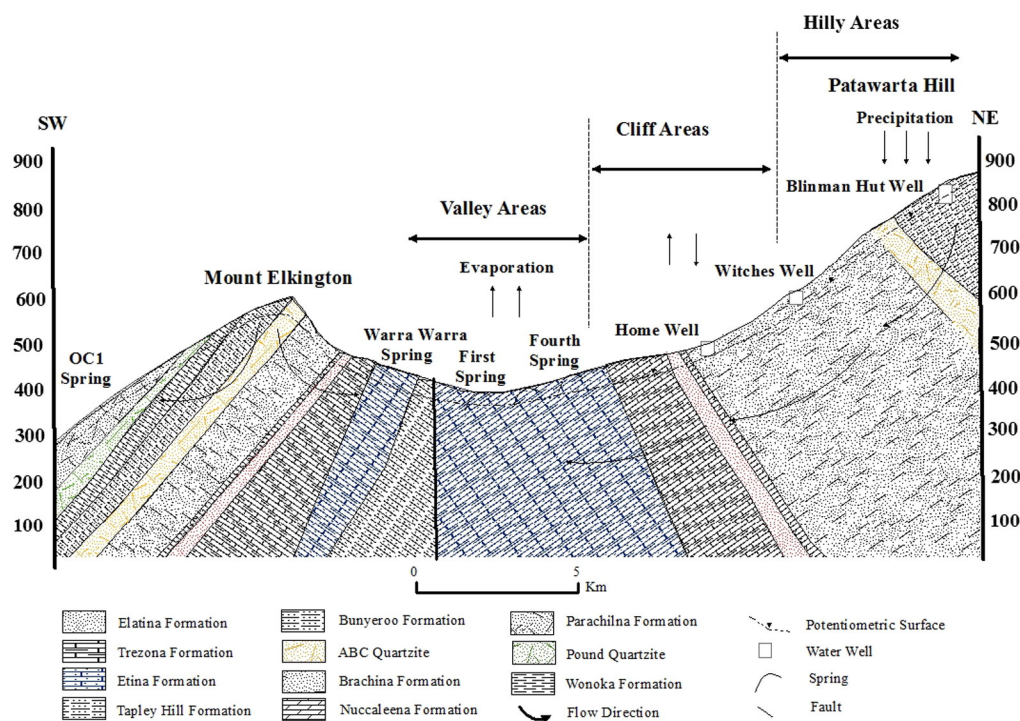


Fig. 13. Conceptual diagram of groundwater flow in the Oratunga Area, Locations of the flow lines are shown in Fig. 4.

neutralization process. These processes increase the calcium and sulfate concentrations dissolved in groundwater which is evident along the flow of groundwater. The high sulfate in both low and high salinity water indicates that pyrite oxidation is significantly important to the chemical evolution of the groundwater.

Based on the isotopic and chemical analysis of groundwater, a conceptual model of groundwater flow was developed to understand groundwater evolution in the study area (Fig. 13).

The Oratunga Area is typical of such a hydrologic system: termed mountain front recharge sedimentary basin. Thus, diffuse recharge of low relief basin is often controlled by low rainfall and a high potential for evaporation from deep zones. While, the adjacent mountain ranges have higher rainfall and lower temperatures with shallower soil profiles attributes that reduce the potential for evaporation and permits dilution, while enhancing rates of direct rainfall recharge and streambed recharge of shallow sedimentary and fractured rock aquifers (Wilson and Guan, 2004). Two possible hydrogeological processes can be distinguished that determine the hydrological function in the study area (Fig. 13): (1) Fractured Rock: water follows regional and local fracture system. The abundant precipitation in the mountains and high density of fractures allow infiltration and comprise the main source of groundwater recharge in area (rapid and direct). This infiltrating water dissolves mainly carbonate and silicates minerals. Therefore water with a predominantly bicarbonate signature is found in these areas. In case of the regional fracture system and the hydraulic connection of the different units, the groundwater flows from marginal areas through mountainous and hilly areas and enters the valleys. During this process, aquifer material is dissolved into the groundwater with low TDS. Due to the rapid groundwater flow, dissolution is possible the dominant process affecting the evolution of groundwater. In absence of the hydraulic connection, local fracture system seems to be the main controlling factor allows lateral flow to act as the primary source of groundwater recharge, whereas local precipitation is insignificant. (2) Groundwater Discharge and Sub-surface Flow.: While in lower topographic and discharge areas, only a little amount of the precipitation that recharging groundwater. Water-rock interactions and the leaching of soluble salts, from the unsaturated zone lead to high concentrations of dissolved

ions in groundwater. The evaporation and ion exchange are considered the dominant processes. As a result, sodium chloride waters are predominant in these areas (diffusive recharge).

7. Conclusion

The hydrological and hydrochemical methods were combined to understand the recharge areas, flow path, and geochemical processes in the Oratunga Area. The groundwater flow seems to follow SSW and NNE directions from the recharge areas to the central and discharge areas. The chemical relations define significant hydrochemical trends and facies in this area. The mixed ion facies and low TDS that generally represent the recent meteoric recharge occur in the higher areas and the chloride facies with high TDS groundwater controlled and influenced by the input of ions along flow process in the lower areas. The ionic ratios results show that the main reactions controlling the groundwater chemistry can be explained by the weathering of carbonates and silicates controlled by soil zone CO_2 , the dissolution/precipitation of calcite, and cation exchange. The major chemical species from these sources are Na^+ , Ca^{2+} , Mg^{2+} and HCO_3^- . The evolutionary trend for the groundwater was relatively consistent along the proposed flow path. A geochemical model was used to confirm the chemical processes using the compositional differences between water points on a flow path. The model was completed within the constraints of minerals and mass balance modelling and the results are consistent with other chemical results from arid areas around the world. In this particular case, the hydrochemical zoning and geochemical evolution identified within the Oratunga Area are of interest for development in the groundwater flow system, which are of major economic importance in the Flinders Ranges region.

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