Surface-groundwater hydrological interaction: An isotope geochemical case study on the Bird in Hand mine South Australia

Thesis submitted in accordance with the requirements of the University of Adelaide for an Honours Degree in Geology – Environmental Geoscience

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THE UNIVERSITY
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SURFACE-GROUNDWATER HYDROLOGICAL INTERACTION: AN ISOTOPE GEOCHEMICAL CASE STUDY ON THE BIRD IN HAND MINE SOUTH AUSTRALIA

AN HYDROLOGICAL STUDY OF A MT. LOFTY RANGES ECOSYSTEM

ABSTRACT

Isotopes of Hydrogen (δ D), Oxygen (δ ^{18}O) and Strontium (^{87}Sr/^{86}Sr) were used as geochemical tracers to build a better understanding of the groundwater system impacting the Bird in Hand mine and its interactions with seasonal rainfall variation and surface processes. These isotopes were used to investigate the dependency of surface vegetation on aquifer waters and rain/soil water, particularly local Eucalyptus species. Isotopes were used to build a better understanding of the interconnectivity of this groundwater system, and the relationships between water sources at different depths and geographical locations. Groundwater from seven bore locations, rainwater sampled over two collection periods, soil and tree samples were taken. It was found that the aquifer accessed by BHMO3 bore is a slow recharging, deep water source with little connection to surface rainfall and nearby bores. The mineralogy at this site changes little from the groundwater level to the surface at this site, and the trees access a Sr source with no input from atmospheric sources. Waters accessed by BH36 bore showed greater influence isotopically from seasonal shifts in rainfall isotopic composition, indicating a greater interaction with surface water/rainfall. Eucalypts at BH36 may access groundwater sources through the extensive fracture system around this site, do not access Sr from the surface soil layers and receive little input from atmospheric Sr sources. All shallow bores sampled access waters that show seasonal trends in isotopic composition following rainfall. Eucalypts at shallow groundwater sites appear to be accessing a mix of sources for Sr, indicating changes in depth of nutrient uptake which may be seasonal and indicate groundwater dependence, although this requires further investigation. The waters accessed by the shallow bores are isotopically distinct from those of the deeper bores, while BH36 and BHMO3 show differing water-isotope patterns, indicating that there is little to no connectivity between the two sites.

KEYWORDS

Determining dependence, aquifer, hydrology, isotopes, 18-Oxygen, Deuterium,

Strontium, Eucalypts, groundwater, Mt Lofty Ranges, geochemistry

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INTRODUCTION

Recognized groundwater dependant systems cover approximately 5% of Australia, yet with the low summer rainfall and regional drought periods characteristic of the continent, groundwater supplied systems have an ecological importance far greater than their somewhat limited geographic extent (Hatton, Evans, & Merz, 1998). Hence, in situations where ground water is extracted from aquifers, such as mine site development and dewatering, having an understanding of an ecosystems' dependence on ground water is critical for determining sustainable levels of water extraction. However aquifers are not simple heterogenic layers of permeable rock, but complex interactions between surface flows, rainfall, the upper alluvial layer and the underlying geology of the area. Therefore sustainable mineral extraction and water usage requires in depth understanding of the complexity of the ground water systems – the geology, recharge systems, depth to water and temporal interactions with the vegetation on the surface.

The Bird in Hand (BiH) gold mine is located 2.7km east of Woodside in the Western Mount Lofty Ranges, South Australia, near the geographic boundary between the Eastern Ranges and Western Mt Lofty Ranges. An historical mine site, workings were inhibited due to groundwater inflows from a Fractured Rock Aquifer (FRA). The site has been recently acquired by a new owner with plans to re-open and de-water the mine to begin further mineral extraction. This paper forms part of the ground water-impact assessment for the BiH project, addressing the reliance of keystone *Eucalyptus* species on groundwater sources, and to build further knowledge regarding the groundwater system impacted by the Bird in Hand mine. To this end, stable and radiogenic isotope geochemistry was employed with three key aims:

1. Determine if the FRA impacting the BiH mine is an interconnected system or a series of isolated water bodies.

2. Determine if the aquifer waters differ significantly from rainwater/soil water in terms of their isotope geochemistry.

3. Determine if the overlying keystone *Eucalyptus* species within the Native Vegetation Heritage Agreement (NVHA) area depend upon groundwater sources to grow and survive.

Figure 1: Location of the study site in South Australia (SA)

Figure 2: Location of site in reference to Woodside Township

Figure 3: From Golder associates Groundwater Assessment (2017), showing the NVHA area (Green), old mine workings (black) and the mine site (purple).

Site History

The BiH gold deposit was first mined in the 1880's and was the largest and most profitable of 17 gold mines in the Woodside goldfield, which produced over 850 kg of gold between 1881 and 1889 (Akker & Watson, 2017). The Bird in Hand Mine produced 298 kg of gold at an average grade of 12.9 g/t in the late 1800's, and progressed to a vertical depth of approximately 110 m. Workings were unable to continue as the shafts broke into a large water bearing fracture, and the subsequent inflows were difficult and uneconomical to manage with the technology of the time. The mine was re-opened and dewatered twice during the 1890s, but financial issues continued to impact the site, and little mineral extraction was carried out. Water from the aquifer has been utilised henceforth for agricultural purposes and by the commonwealth directly to supply a nearby army barracks from 1933 until 1966. Dewatering occurred again in 1933, with prospecting and mine and shaft extensions occurring until 1939 (Akker & Schneyder, 2017). The next dewatering and mine re-opening is set to occur before the end of 2021.

Much of the area overlying the site has been a designated Native Vegetation Heritage Agreement (NVHA) area since 2015. Eucalyptus *leucoxylon* (from here on Blue Gum) and Eucalyptus *camaldulensis* (from here on Red Gum) are keystone species that provide habitat for a number threatened fauna and flora species, including several native orchids and declining Mount Lofty Ranges region avifauna, that are found in the understory and canopy (Akker & Schneyder, 2017). Eucalyptus species, particularly Red Gum, are often very groundwater dependent, as evidenced by the extensively distributed stream/creek side red gum communities in the dry interior of the country that depend almost entirely on groundwater (Hatton et al., 1998). Even in higher rainfall areas with greater surface and rainwater availability, many tree species (including eucalyptus species, particularly Red Gum) have been shown to preferentially source groundwater over surface, stream and soil water (Adar, 1995; Dawson, 1991; Thorburn, Mensforth, & Walker, 1994). Furthermore, these species can change their primary water source during times of drought or otherwise low water availability, such as seasonal variation in rainfall (Dawson & Pate, 1996; Eamus, Froend, Loomes, Hose, & Murray, 2006).

If the projected mine dewatering were to go ahead, current groundwater Standing Water Levels (SWL) will decrease. If the surrounding surface vegetation relies at least partly on the affected groundwater sources this would have a proportional negative impact on the trees and ecosystem at large, particularly during dry periods. There is therefore a need to understand the interactions between the groundwater and the surface vegetation, and how the groundwater system as a whole will be impacted by dewatering processes.

GEOLOGICAL SETTING AND SITE BACKGROUND

The aquifer system impacting the mine site is a Fractured Rock Aquifer (FRA) consisting of five main hydro-stratigraphic units: the Tapley Hill Formation, Brighton Limestone (marble), Tarcowie Siltstone, Cox Sandstone and the Kanmantoo Formation further east of the catchment (Whittaker, 2017).

The proposed workings aim to access the deepest parts of the marble that contains the gold deposit. Below the Brighton Limestone and outcropping to the north and west is the Tapley Hill Formation, which is the unit that supports the majority of groundwater users. An upper zone of highly weathered siltstones with interbedded, minor fine grained sandstones within the Tapley Hill Formation creates an aquitard which underlies the majority of the NVHA area. This weathering reaches a depth of 90m directly adjacent to the orebody, with intensity and depth decreasing with distance from the orebody (Akker & Schneyder, 2017). Overlying these units is the Tarcowie Siltstone interbedded with the Cox Sandstone Units. The Tarcowie Siltstone was examined through exploration and investigation wells, which intercepted the significant fracture zone in the hanging wall. The fracture had a measured groundwater yield of up to 40 L/s. The FRA in total has groundwater supply rate capabilities of 1-40 L/s at depths of <200m. Measured salinities range from less than 1,500 mg/L up to 4000 mg/L to the east, in the less productive and older Kanmantoo Formation.

Groundwater receptors for this FRA within the Inverbrackie sub-catchment include several operational wells and the Inverbrackie Creek, which receives baseflow in the lower reaches, mostly during winter when the groundwater levels are higher.
The fracture zone has transmissivity of 67 m^2/day (geometric mean) and is the most significant mode of groundwater flow into the mine if intercepted by mine workings. Depth to water below ground level (bgl) varies. Approx. 90% of the NVHA area has a depth to water of 20-60m bgl, the other 10% a depth of ~10-15m bgl (Akker & Watson, 2017).

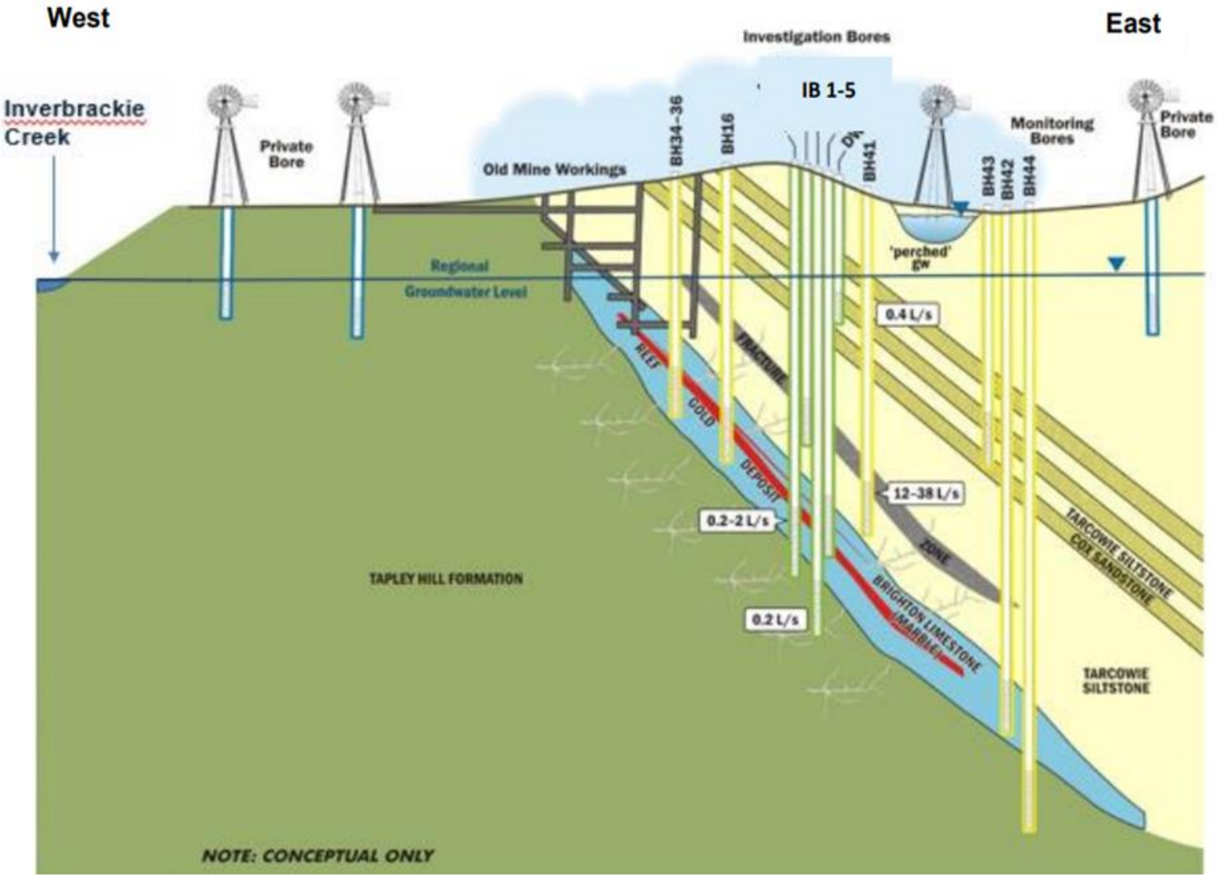


Figure 4. Conceptual model diagram of the groundwater interactions with the investigation bores and mine workings. Note the BH34-BH36 bore depths and interactions, as BH35 and BH36 were sampled during this study.

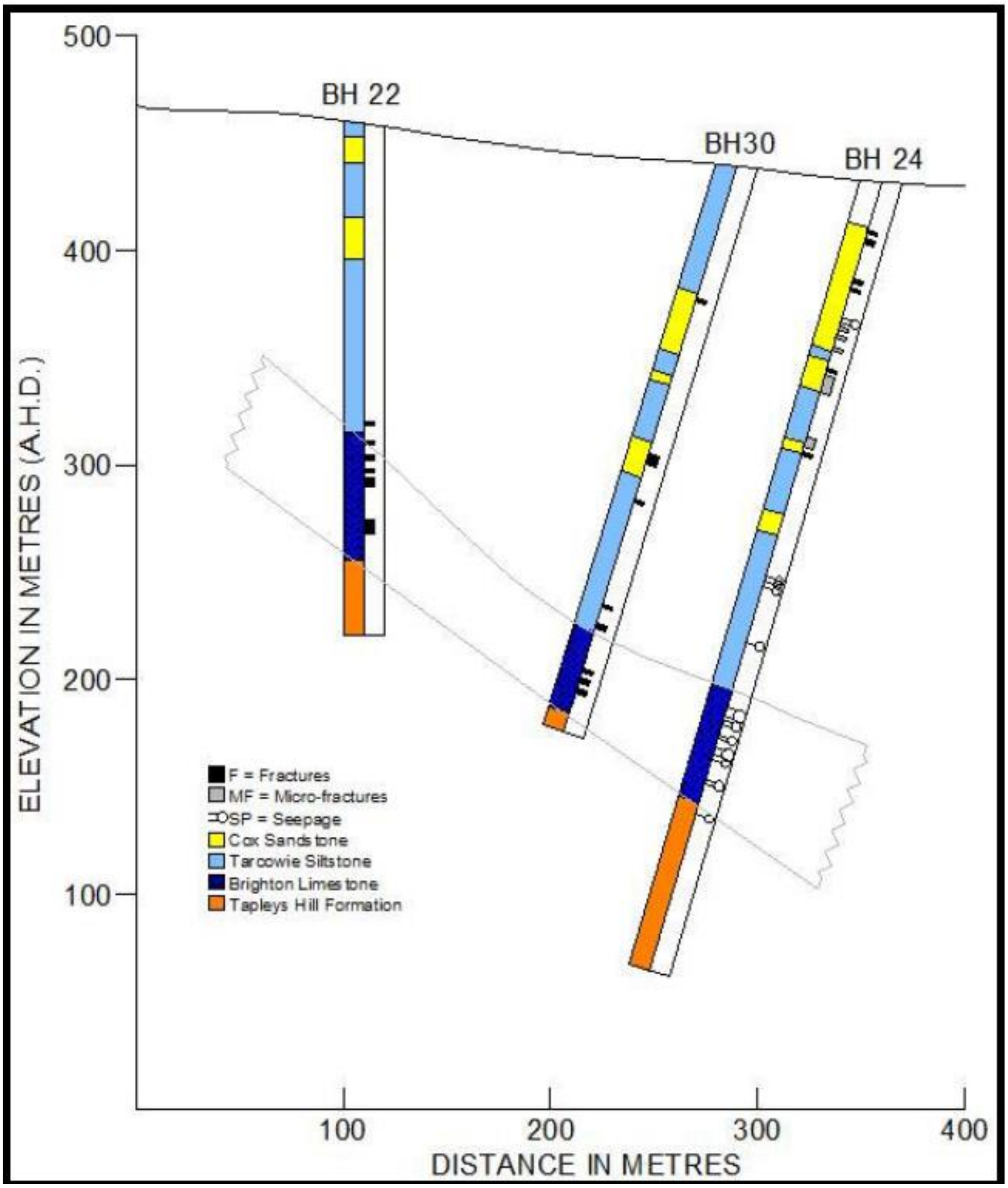
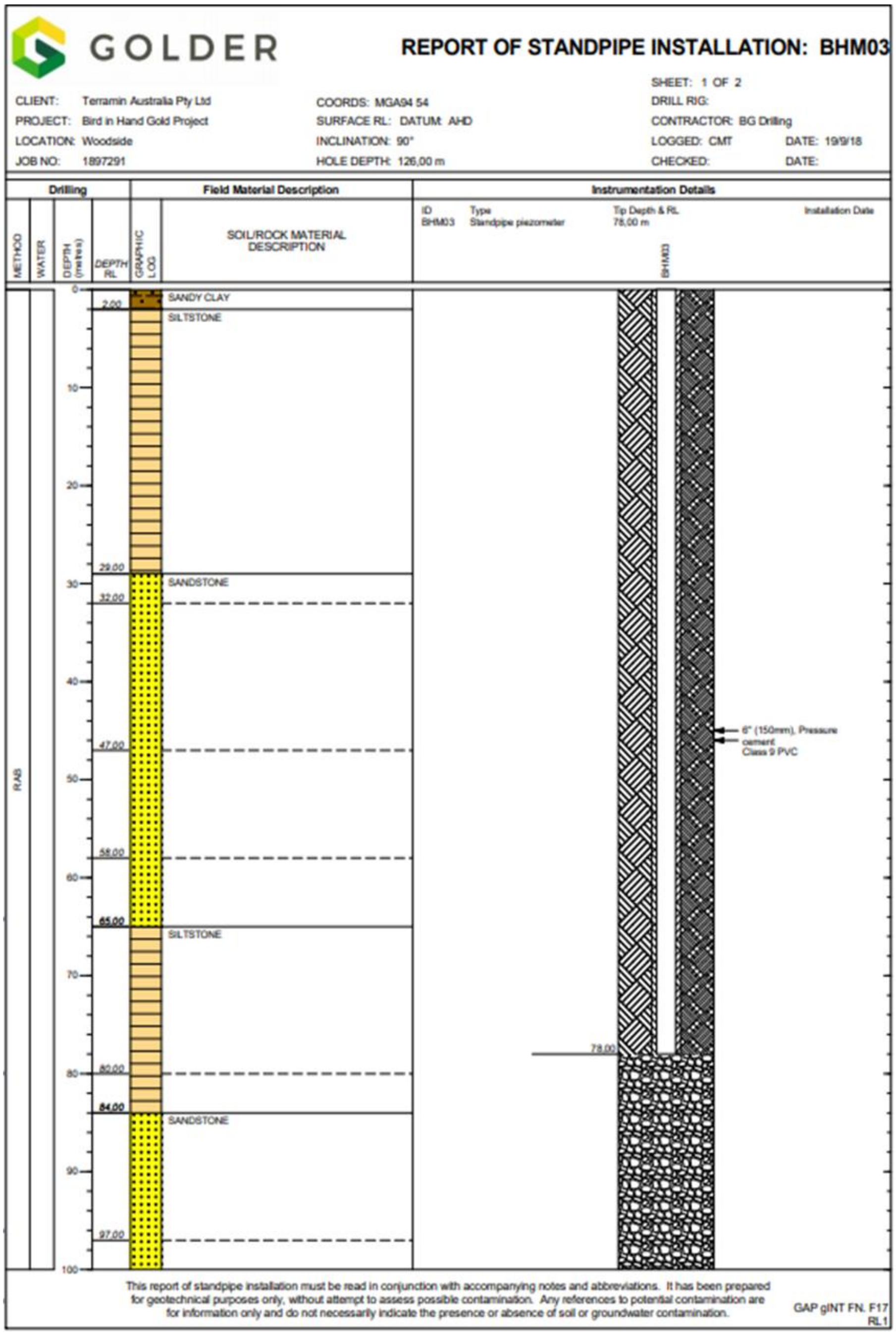


Figure 5: Conceptual model of the hydro-stratigraphic units observed at the site from investigation well drilling observations of bores in the NVHA. These bores are in close proximity (<200m) to the bores sampled in this study. From Aquaterra (2008) .



GOLDER

REPORT OF STANDPIPE INSTALLATION: BHM03

SHEET: 1 OF 2

CLIENT:	Terramin Australia Pty Ltd	COORDS:	MGA94 54	DRILL RIG:	
PROJECT:	Bird in Hand Gold Project	SURFACE RL:	DATUM: AHD	CONTRACTOR:	BG Drilling
LOCATION:	Woodside	INCLINATION:	90°	LOGGED: CMT	DATE: 19/9/18
JOB NO:	1897291	HOLE DEPTH:	126,00 m	CHECKED:	DATE:

Instrumentation Details

ID	Type	Tip Depth & RL	Installation Date
BHM03	Standpipe piezometer	78,00 m	

This report of standpipe installation must be read in conjunction with accompanying notes and abbreviations. It has been prepared for geotechnical purposes only, without attempt to assess possible contamination. Any references to potential contamination are for information only and do not necessarily indicate the presence or absence of soil or groundwater contamination.

GAP gINT FN. F17
RL1

Figure 6: Standpipe installation report for BHMO3 showing the stratigraphic units and bore-hole casing characteristics.

δ ^{18}O and δ ^{2}H

In the dry Australian conditions, it has been found that if an ecosystem in Australia exists in the presence of available groundwater, it is unlikely that there will be no dependence on it If the groundwater were made to be less available due mine development/water extraction, the system would suffer. The key is to identify to what degree the system is dependent upon groundwater sources and understand the potential effects on the ecosystem should this groundwater source become unavailable. The use of water isotopes (namely oxygen-18 and deuterium) to investigate the source water of trees is well established (Dawson, 1991; Eamus et al., 2006; Thorburn et al., 1994). As the uptake of water by tree species into xylem sap is non-fractionating until it reaches tissues undergoing water loss, isotopic analysis of xylem fluid can be performed to reliably infer water uptake pathways in a non-destructive manner (Ehleringer & Dawson, 1992). This is only possible if the rainwater and groundwater have different isotopic signatures, and if the soil water has a changing isotopic signature with depth. There are mechanisms that create differences in the isotopic signature of water bodies depending on a number of factors. The delta Deuterium (δD, δ ^{2}H) and delta ^{18}O (δ ^{18}O) of a water body are reflective of its meteoric origin, its exposure to evaporation and soil movement, and its recharge points and sources. If there is mixing between sources, this will influence the signature. Groundwater recharge occurs through either or both indirect recharge (inflow from streams or depressions) and direct recharge through the surface materials (Barnes & Allison, 1988). Direct recharge tends to create the most abrupt changes in isotopic signature between groundwater and rainfall, as there are isotopic changes with depth through the unsaturated zone due to a number of factors outlined by Barnes and Allison (1988). The isotopic composition of rainfall varies geographically, due to orographic influences, temporally/seasonally and through specific weather systems and events (Guan, Simmons, & Love, 2009; Guan, Zhang, Skrzypek, Sun, & Xu, 2013). If there are differences in the isotopic signatures for oxygen and hydrogen between groundwater and rainwater observed at this site, than isotope analysis can performed on the potential source waters to build a better understanding of recharge rates, fracture connectivity and recharge pathways of the FRA system, and on xylem and soil waters to identify the source waters of the Eucalypts.

$^{87/86}$Sr as a hydrological tracer

The radiogenic isotope for Strontium, ^{87}Sr, is generated by the emission of a negative Beta-particle from ^{87}Rb and the ratio of ^{87}Sr/^{86}Sr can be measured using thermal ionisation mass spectrometry. The ^{87}Sr/^{86}Sr ratio depends on the water body or rock's initial composition and the amount of radiogenic Sr generated from decay of 87Rb over time (Veizer, 1989). The ^{87}Sr/^{86}Sr ratio of rocks varies significantly and depends on their geological regime with potential geographical variations in the Sr contents caused by mixing of Sr with different isotopic values. Hence, the ^{87}Sr/^{86}Sr ratio of groundwater is dependent upon the composition and age of surrounding rock types, the flow pathway of water into the aquifer, and the residence time and recharge rates of water in the system. Some examples of using the ^{87}Sr/^{86}Sr signature of water have been to investigate the residency of groundwater pools, groundwater influence on flooding and base flow of streams, and erosional pathways (Blum, Erel & Brown, 1994; Land, Ingri, Andersson, & Ohlandera, 2000; Negrel, Allegre, Dupre, & Lewin, 1993; Négrel & Petelet-Giraud, 2005). The rocks underlying the NVHA represent a series of formations of differing composition, depths and ages (Whittaker, 2017). Hence Sr isotopes, along with δ D and δ ^{18}O, will be used to determine if the FRA underlying the mine represents a series of isolated aquifers lying at different depths and locations, or a large, interconnected network of groundwater storage points, recharged by the same pathways and lying at similar depths.

The bioavailable Sr in a given area derives both from geological weathering of local bedrock and atmospheric input. Bioavailable Strontium is Sr in water soluble forms, and is derived from both weathered bedrock/soil sources and atmospheric input (Nakano, Tanaka, Tsujimura, & Matsutani, 1993). The $^{87}Sr/^{86}Sr$ ratio of rainfall has been found to be mostly representative of soluble atmospheric input (Capo & Chadwick 1999) and so it is assumed that the rainfall Sr is representative of bioavailable atmospheric Sr inputs at this site. The atmospheric input of Sr into soils is deposited onto the surface, whereas weathering releases Sr from minerals from within the soil horizons, and so the bioavailable Sr isotopic ratio may form a depth gradient, trending away from atmospheric to bedrock signals (Poszwa et al., 2004). Therefore, the $^{87}Sr/^{86}Sr$ ratio of tree wood and leaf material is dependent upon surrounding geology and hydrology, atmospheric inputs from dust and rainwater, and the primary depth of nutrient uptake (Capo, Stewart, & Chadwick, 1998; Nakano et al., 1993; Vitousek, Kennedy, Derry, & Chadwick, 1999).

It was hypothesised that the potential source waters for vegetation in the study area - groundwater and rain water, were to have distinct isotopic signatures, and that this data would provide insight into the hydrology and eco-hydrology of the ecosystems within the NVHA and surrounding mine site.

METHODS

Sample collection

All sampling was conducted approximately bi-monthly from February 2019 to the end of July 2019. All collected samples were stored in a refrigerator at < 5 degrees Celsius within half a day of collection until their analysis.
Groundwater collection was performed using a hand bailer at a series of monitoring bores in and around the NVHA. The bailer and the collection bottles were both rinsed with bore water from each sample site three times prior to filling and capping the collection bottles. Depth to water was recorded at each location using a water level dipper. Each location is marked on the map (Figure 1).

Rain water collection began from 21/03/2019 to the 29/05/2019. A second rainwater collection was undertaken from 29/05/2019 to 31/07/2019. The collector was located at the BiH mine site, an image of its configuration is shown in Figure 2.

Soil sampling was performed at each tree sample location. Samples were taken with an hand auger at three depths (15-35-50cm), and each sample was double bagged and stored, although only the 35-50 cm segment was analysed for Sr. Soil and tree (leaf) samples marked Goldwin Creek were taken from the closest, large and established solitary Red Gum (*Eucalyptus camaldulensis*) to the bore, which was a several hundred meters from the bore site. Soil and tree samples for Cow Calf bore were taken from the closest grove of Eucalypt trees to the north-east of the bore across the vehicle track. All other soil and tree samples were taken directly adjacent to the sampled bores. Trees sampled were all large, well established Blue gums (*Eucalyptus leucoxylon*) and Red gums. Tree core samples were taken using a hollow-drill bit. Stem and leaf samples were taken from each sampled tree, except at BH36, where the height of the trees limited access to healthy leaves, and so only core samples were taken. All samples were double bagged at site and stored in the refrigerator at < 5 degrees C. The ends of all stem samples were then covered in hot glue to prevent evaporation and stored again in the refrigerator.

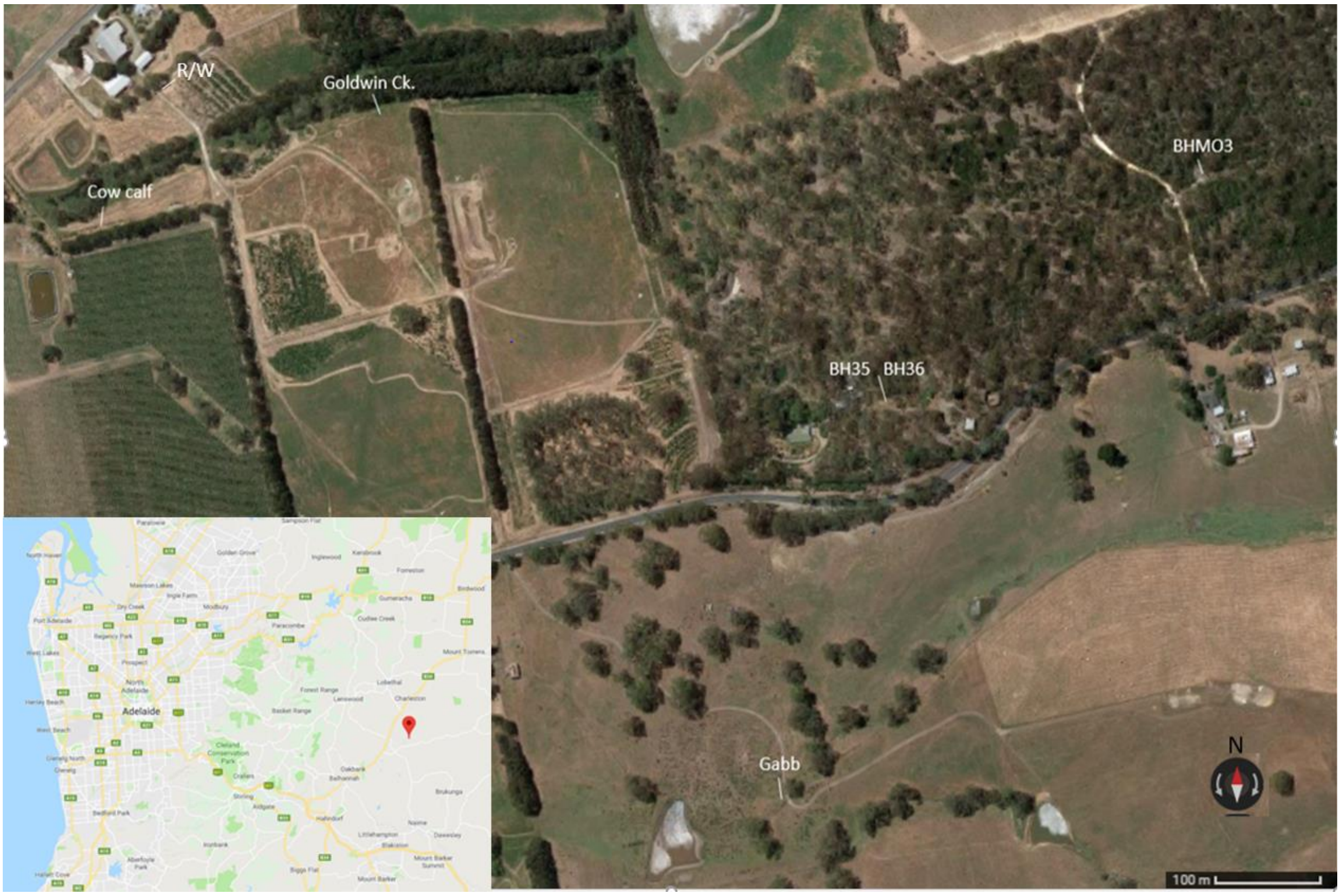


Figure 7: Map showing the geographical location of the sampled bores. Goldwin R/W tank and the storage tank for the Goldwin Op. Bore were located in the collection of buildings to the north of Cowcalf bore. The rainwater collector is marked as R/W

Figure 8: The rainwater collector used in this study, a lab cleaned bottle with a layer of paraffin oil to prevent evaporation, wrapped in reflective material to further reduce evaporation. The funnel was filtered using slitted plugs to prevent sediment contamination. The black spikes are to prevent perching birds.

Water extraction

Water extraction from soil and tree stem samples using cryogenic vacuum distillation was attempted, using a modified version of the method used by Harland (2018). Improvements were made such as seals at the lids of the centrifuge tubes to improve the vacuum and modified cryo-capture loops to improve vapour capture. A detailed description of the processes and images of the set up are available in the appendix A. After stringent testing, this process was deemed insufficient to obtain useful isotope data, particularly for the stem samples. This was due to an insufficient vacuum being created by the pump that was available to use, which exaggerated already contentious issues with the method considered by (Orlowski, Breuer, & McDonnell, 2016; Orlowski, Frede, Bruggemann, & Breuer, 2013; Tsuruta et al., 2019). Hence, data from the use of this method was not utilised in the project.

Strontium

Soil bio-available strontium was prepared for analysis using the method outlined by (Harland, 2018), who in turn used a modified version of the ammonium acetate method from (van Reeuwijk, 2002). A 1 Molar (M) ammonium acetate solution was made up, with 20 ml of solution added to approx. 2gm of soil sample and a blank. Mixed samples were then placed into a rotor shaker overnight, then centrifuged for half an hour. The liquid was then transferred into Teflon and evaporated on a hotplate at 140 degrees C. The sample was then ready for analysis. A series of blanks were run on two different available brands of ammonium acetate in order to find the most suitable solution to use, with the Fisher brand returning the best blank, and so this brand was used to separate bio-available strontium from the soil.

Strontium analysis of tree samples was conducted on fresh leaves from each sampled tree. Leaf samples were washed with ultra clean de-ionised (DI) water and left to dry overnight. All leaf, wood core samples and a blank were then placed into acid cleaned crucibles and incinerated overnight at 550 degrees Celsius. The ashed samples and were then rinsed from the crucibles into Teflon vials using 6M nitric acid, placed on a hotplate to reflux and oxidise organics, then evaporated down and left ready for analysis.

Isotope Analysis

$^{18}O/^{16}O$ and D/H analysis of all water samples was conducted using the Picarro cavity ring-down Water Isotope Analyser at Flinders Analytical, Flinders University. Waters were filtered by nanofiber disposable filters prior to analysis to remove contaminants and organics. All analyses were preceded by a dummy and three standards: Evian, desalinated water standard, and a rain water standard. Each run of samples was then followed by the three standards. Delta (δ) is found from R, which is defined as

$$R = \frac{\text{amount of } H_2{}^{18}O}{\text{amount of } H_2{}^{16}O} \quad \text{or} \quad R = \frac{\text{amount of } HD^{16}O}{\text{amount of } H_2{}^{16}O}$$

And δ

$$\delta^{18}O = \frac{R_{sample} - R_{standard}}{R_{standard}} \cdot 1000‰ \quad \text{or} \quad \delta D = \frac{R_{sample} - R_{standard}}{R_{standard}} \cdot 1000‰$$

Strontium isotope analysis was performed on water, soil and tree samples. Each sample was run through the $^{87}Sr/^{86}Sr$ chromatographic column procedure before being analysed on the ISOTOPX PHOENIX TIMS (Thermal Ionisation Mass Spectrometry) in the Mawson laboratory, University of Adelaide. Each run of samples was accompanied by a TIMS standard, a known $^{87}Sr/^{86}Sr$ spiked procedural blank and an IAPSO Mid-Atlantic Sr standard.

RESULTS

Table 1: Measured δ ^{18}O and δ ^{2}H for rainwater and groundwater, the Standing Water Level (SWL) and average SWL for each site and sampling date. Goldwin Op bore was sampled from a storage tank and so depth was not measured at each date, but is approximately 12m.

δ ^{18}O ‰ and δ 2H‰ data:

Date of collection	Site	δ ^{18}O	δ ^{2}H	SWL (m)	Avg SWL (m)
6/02/2019	BH35	-5.16	-27.98	35.49	
31/07/2019	BH35	-5.10	-27.37	39.55	
6/02/2019	BH36	-2.55	-13.01	36.79	39.9175
21/03/2019	BH36	-5.07	-26.82	40.49	
29/05/2019	BH36	-5.07	-26.88	41.61	
31/07/2019	BH36	-5.13	-27.18	40.78	
6/02/2019	BHM03	-5.46	-29.64	44.53	
21/03/2019	BHM03	-5.44	-29.77	44.54	44.645
29/05/2019	BHM03	-5.46	-29.46	44.67	
31/07/2019	BHM03	-5.47	-29.56	44.84	
6/02/2019	Cow Calf Bore	-4.95	-26.17	15.85	
21/03/2019	Cow Calf Bore	-5.05	-27.10	16.94	
29/05/2019	Cow Calf Bore	-5.04	-27.30	12.15	13.7725
31/07/2019	Cow Calf Bore	-5.26	-28.47	10.15	
6/02/2019	Gabb bore	-5.07	-26.55	9.79	
21/03/2019	Gabb bore	-5.21	-27.67	10.5	
29/05/2019	Gabb bore	-5.16	-27.25	10.1	9.9425
31/07/2019	Gabb bore	-5.24	-27.54	9.38	
6/02/2019	Goldwin Creek Bore	-5.02	-26.77	9.41	
21/03/2019	Goldwin Creek Bore	-5.01	-26.88	8.99	9.3125

29/05/2019	**Goldwin Creek Bore**	**-5.02**	**-26.83**	**9.45**
31/07/2019	**Goldwin Creek Bore**	**-5.20**	**-27.78**	**9.4**
6/02/2019	**Goldwin Op Bore**	**-5.02**	**-26.84**	**12**
21/03/2019	**Goldwin Op Bore**	**-5.14**	**-27.99**	**12**
31/07/2019	**Goldwin Op Bore**	**-5.14**	**-27.38**	**12**
6/02/2019	**Goldwin R/W tank**	**-2.87**	**-12.21**	
29/05/2019	**Rain water**	**-4.92**	**-21.93**	
31/07/2019	**Rain water 2**	**-5.98**	**-30.13**	
31/07/2019	**rain water 2 second run**	**-5.8877**	**-29.539**	

δ Deuterium and δ ^{18}O of Ground and Rain water

Measured δ ^{18}O and δ ^{2}H for rainwater collected on site was δ ^{18}O = -4.92 and δ ^{2}H = -21.93 for collection period 21/03/2019 to 29/05/2019 and δ ^{18}O = -5.98 and δ2H = -30.13 for collection period 29/05/2019 to 31/07/2019. Rainwater collected from the Goldwin Rainwater Tank on 6/02/2019 showed a heavily enriched signal of δ ^{18}O = -2.87 and δ ^{2}H = -12.21.

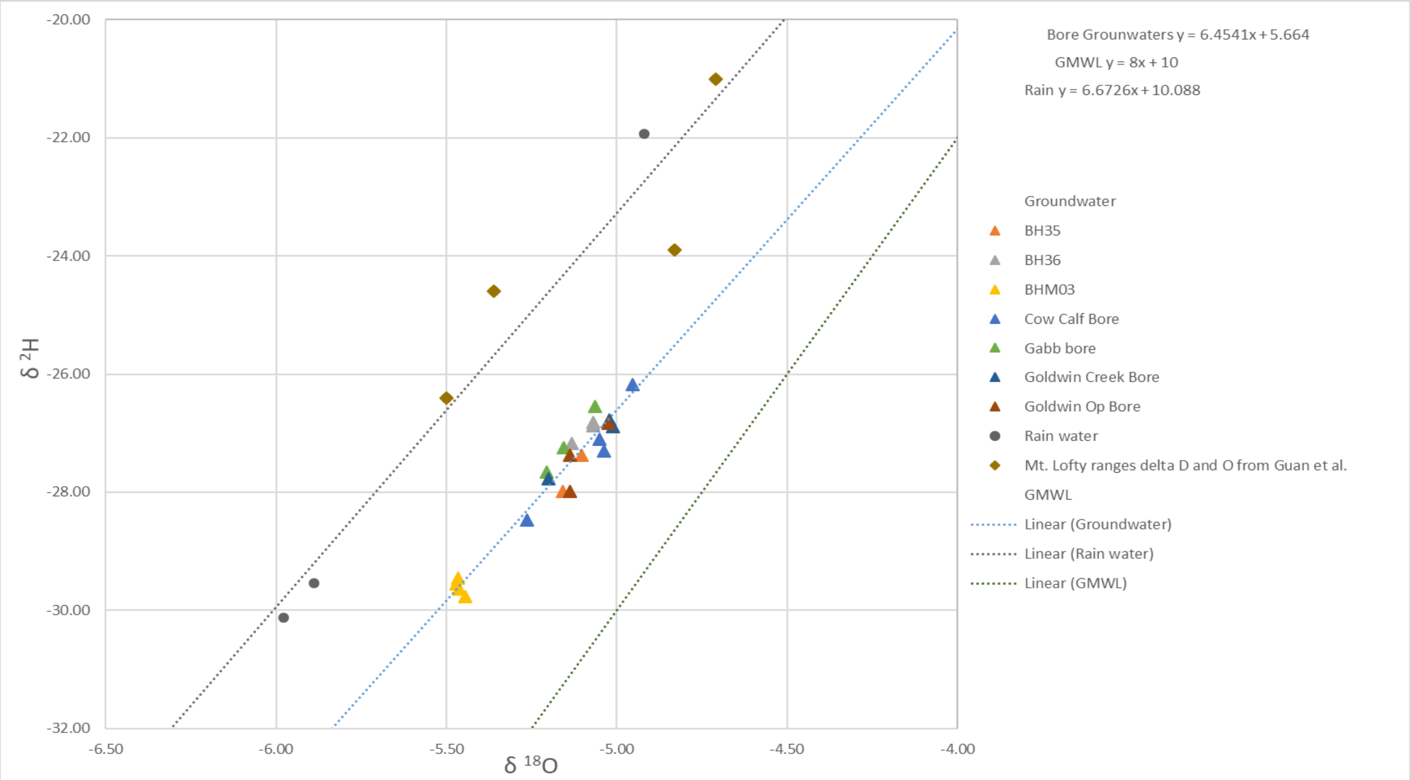
Groundwater signatures varied from site to site, as can be seen in figures 10a and 10b. Cow Calf Bore, had the greatest shift in water isotope signatures for all measured bores, with δ ^{18}O = -4.95 and δ ^{2}H = -26.17 for collection date 6/02/2019 to δ ^{18}O = -5.26 and δ ^{2}H = -28.47 for collection date 31/07/2019, with a trend of more negative values for both δ ^{18}O and δ ^{2}H for each collection date over the sampling period. The most depleted values for groundwater were δ ^{18}O = -5.47 δ ^{2}H = -29.77 for BHMO3, which is the only bore water sampled that did not shift isotopically throughout the sampling period.

Goldwin Creeks had the lowest standing water level with an average water depth of 9.31 m. BHMO3 was the deepest sampled bore with an average SWL of 44.645 m. Cow Calf Bore is another shallow perched aquifer with a SWL that ranged from 16.94m to 10.15m, which is the greatest change in water depth observed from all measured bores.

Some water isotope analysis results produced marked outliers, such as BH36 6/02/2019 which had $\delta\ ^{18}O = -2.55$ and $\delta\ ^{2}H = -13.01$, which is much more enriched than any sample gathered other than heavily evaporated rainwater from the Goldwin water tank at the BiH site, which had values of $\delta\ ^{18}O = -2.87$ and $\delta\ ^{2}H = -12.21$. It is possible that sample BH36 6/02/2019 underwent evaporation in in the sample bottle and has been omitted from the data set due to analytical/human error. Gabb bore 31/07/2019 was flagged by the PICARRO during analysis due to the presence of organic molecules in the water, and although its values are well within the expected range, consideration of its validity should be made when observing this data point in context with the rest of the data.

Figure 10 shows that the shallower bores such as Cowcalf, Gabb Goldwin Operational Bore and Goldwin Creek followed similar trends towards more negative values for $\delta\ ^{18}O$ from 6/02/2019 to 21/03/2019, followed by a maintenance of $\delta\ ^{18}O$ values or slight enrichment (Gabb) until 29/05/2019, aside from Goldwin creek, which considering error stayed consistent from 6/02/2019 to 29/05/2019. From 29/05/2019 to 31/07/2019 all shallow sample sites showed a sharp negative trend, with Cowcalf, Gabb and Goldwin Creek all showing their lowest values measured at this time although Goldwin op bore changed little between 21/03/2019 and 29/05/2019. Similar trends were observed for $\delta\ ^{2}H$, with nearly identical trend lines appearing for both signatures, yet the groundwater values for all bores other than BHMO3 are much closer to the rainwater $\delta\ ^{18}O$ at 29/05/2019 than at the end of the sampling period, while the opposite is true for $\delta\ ^{2}H$. The deeper bores, particularly BHMO3 showed the least change in both variables over the course of the sampling period. Rainwater went from showing the most enriched values measured at the first collection date, to showing the most negative for both ^{18}O and Deuterium at the last collection.

Figure 9a.



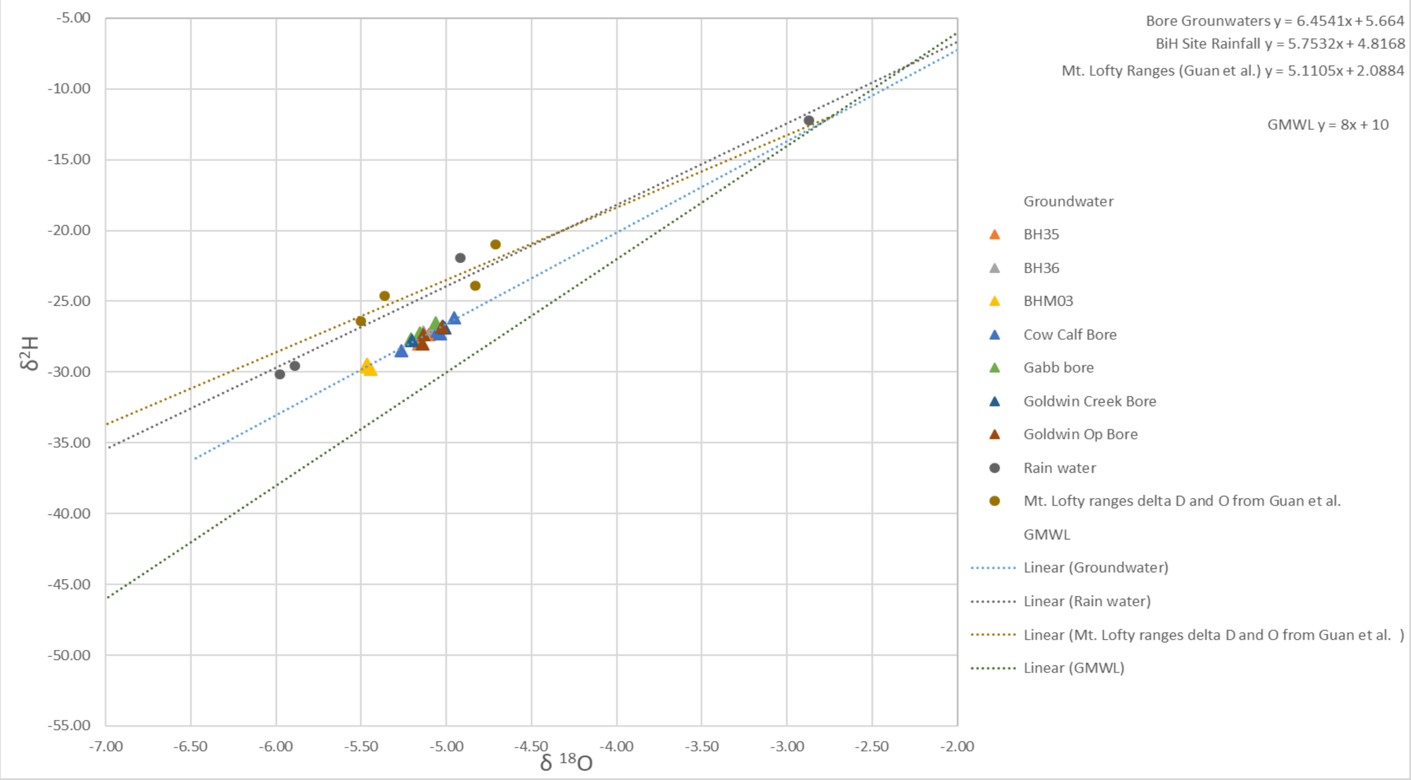
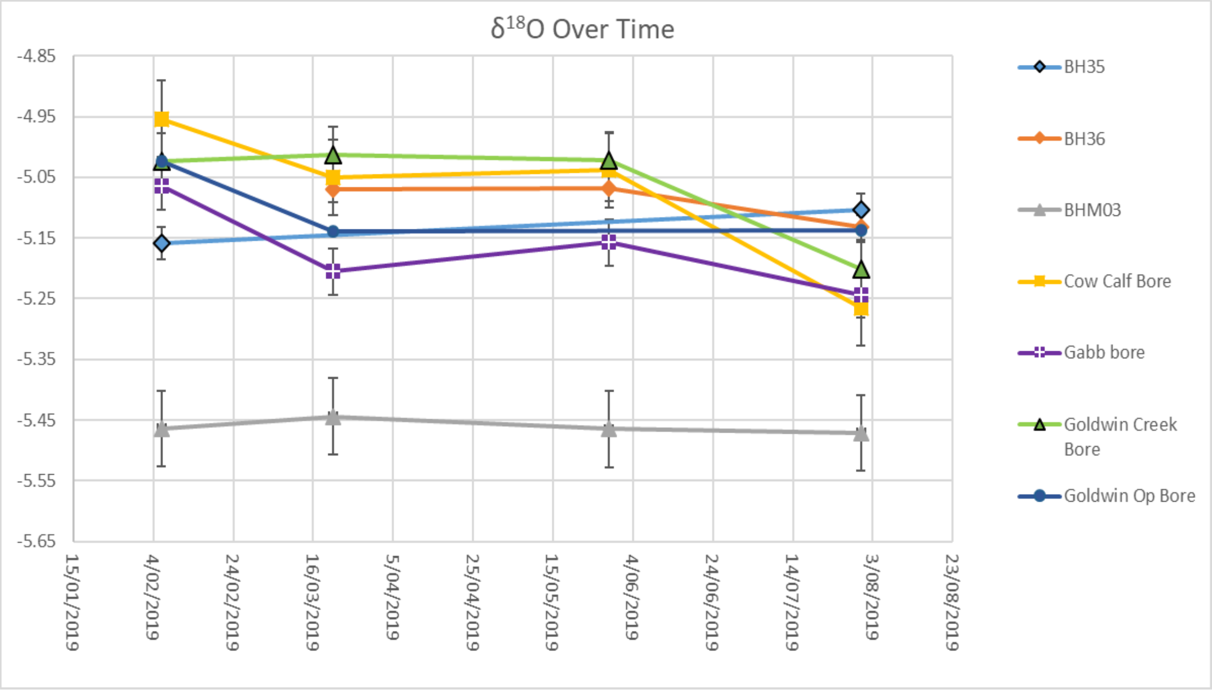


Figure 9b

Figures 9a – 9b: Scatter plot with trend lines for Rain and Groundwater plotted against the Global Mean Water Line (GMWL) and previous Mt. Lofty ranges data from Guan et al (2009).

Figure 10a



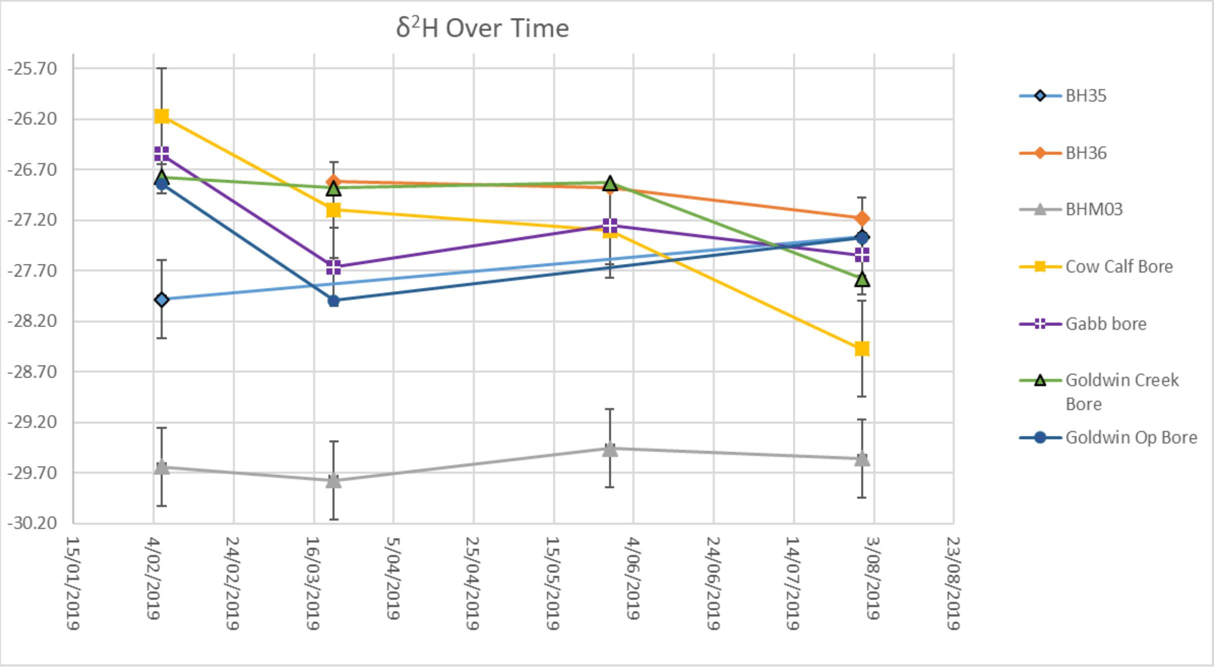


Figure 10b

Figure 10a – 10b: Graphs of the trend of δ ^{18}O and δ ^{2}H values of groundwater for each bore site over the sampling period.

Strontium isotopes

Table 2: Table of results showing the $^{87/86}Sr$ signals from each sample site and type, along with analysis error. Note that the final sample (G/w Ck. Soil) has a very large error and was run twice, with slightly different values on the second run. The large error sample is not included in any analysis.

Sample ID	Mean (After) $^{87/86}Sr$	Error
BH35 6/02/2019	.714069	.00021
BH36 21/03/2019	.713757	.00021
BH36 29/05/2019	.713796	.00018
BH36 6/02/2019	.713829	.00021
BH36 soil	.715049	.00028
BH36 Woodcore	.713670	.00025
BHMO3 21/03/2019	.713649	.00024
BHMO3 29/05/2019	.713597	.00024
BHMO3 6/02/2019	.713690	.00023
BHMO3 soil	.713504	.00019
Sr leaf BHMO3	.713515	.00017
Cow calf Bore 21/03/2019	.715610	.00024
cow calf bore 29/05/19	.715726	.00021
Cow calf bore 6/02/2019	.715400	.00024
Sr leaf Cow calf	.713691	.00020
Cow calf soil	.713301	.00017
Gabb Bore 21/03/2019	.714499	.00023
Gabb bore 29/05/2019	.714479	.00022
Gabb Bore 6/02/2019	.714479	.00026
Goldwin Creek 29/05/2019	.715119	.00023
Sr leaf G/W Ck	.712843	.00023
Goldwin Creek Bore 21/03/2019	.715027	.00020
Goldwin Creek Bore 6/02/2019	.714845	.00022
G/w Ck. Soil	.713054	.00024
Goldwin op Bore 21/03/2019	.715024	.00022
Goldwin op Bore 6/02/2019	.715023	.00023
Goldwin R/W tank 6/02/2019	.711026	.00018
Sr Rain 29/05/2019	.710906	.00023
G/w Ck. Soil	.714108	.11757

Groundwater Strontium

All $^{87/86}$Sr data and error for groundwater, soil and tree samples can be found in table 2. Figure 11 shows the data with their errors, and along with figure 9 demonstrates that there are distinct differences in $^{87/86}$Sr between the deeper bores BHMO3 and BH35/36 and the shallower water storages accessed by Cowcalf Bore, Goldwin Creek, Goldwin operational bore and Gabb bore.

Rainwater sampled from the rainwater tank on site and rainfall collected in the rainfall collector from 21/03/2019 to 29/05/2019 showed values for $^{87/86}$Sr that are well within error of each other, and very distinct from all other samples collected, with values of 0.711026 and 0.710906 respectively.

BHMO3 had the lowest average at $^{87/86}$Sr 0.713645, followed by BH36 0.713794, BH35 0.714069, Gabb bore 0.714485, Goldwin Creek 0.714997, Goldwin Op. 0.715024 and Cow Calf 0.715578952.

In contrast to the water (O and D) isotope values, the $^{87/86}$Sr signals for samples taken from each site exhibited no change from summer to winter 6/02/2019 - 31/07/2019.

Soil Strontium

Bioavailable soil $^{87/86}$Sr varied from site to site, and exhibited values from largest to smallest BH36 soil 0.715049, G/w Ck. Soil 0.714108, BHMO3 soil 0.713504, Cow calf soil 0.713301, G/w Ck. Soil 0.713054 (Figures 8 and 10). All soils were distinct from rainwater, with BH36 being the most separated from rainwater. BHMO3 soil Sr was within error of the groundwater signal from the site, while all other sites had a soil Sr signature distinct from their respective groundwaters, with the shallow bores soil Sr below the groundwater, while BH36 soil had a higher value than the site's groundwater.

Leaf and wood core strontium

The leaf strontium isotopes varied from site to site, with leaf samples from Goldwin Creek 0.712843 and Cow Calf 0.713301, BH36 Wood core 0.713670 and BHMO3 0.713504.

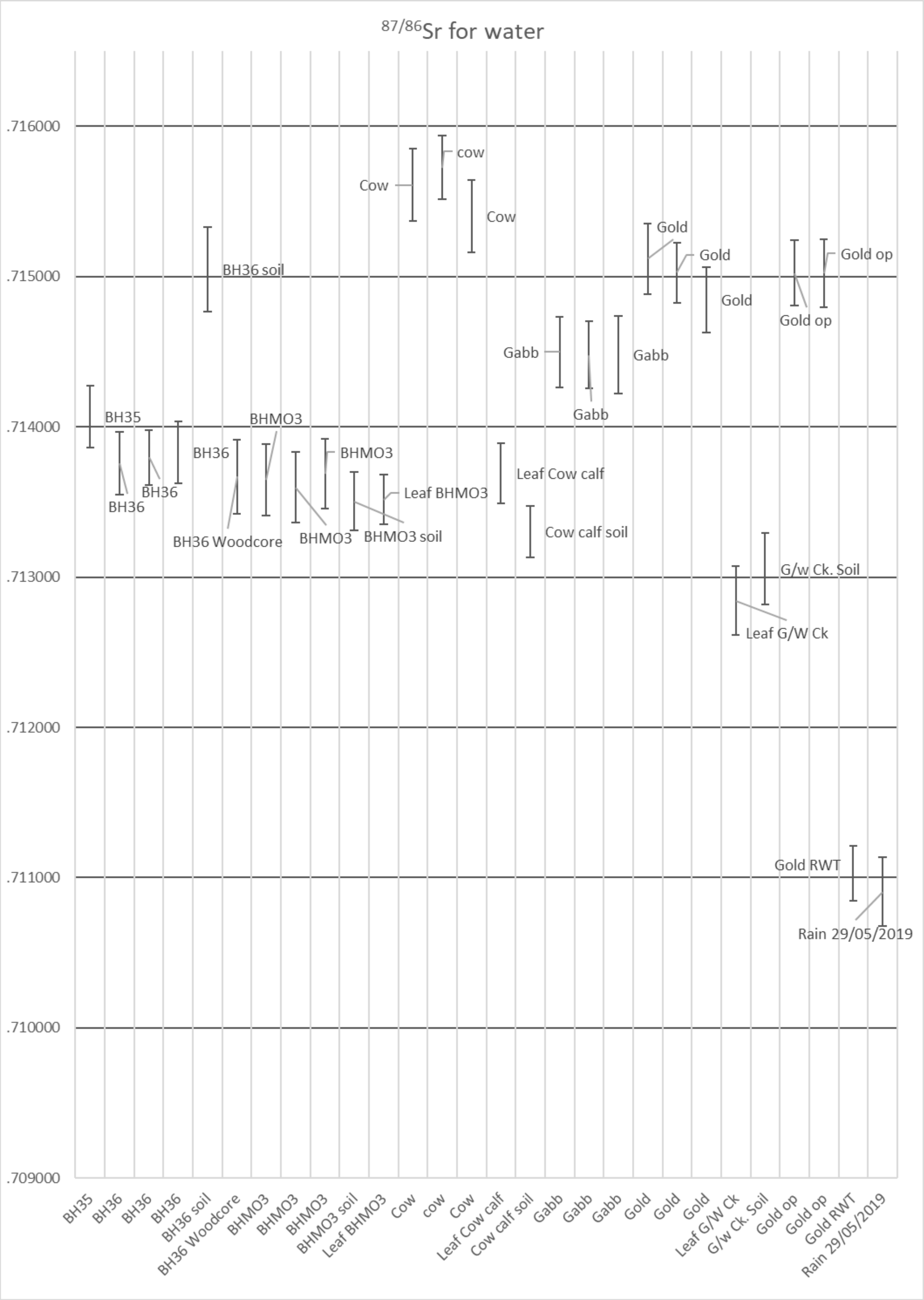


Figure 11: Shows the Strontium isotope data with their errors, organised such that differences in values between sample type and location can be easily observed. Cow – Cow Calf Bore, G/W creek – Goldwin Creek Bore, Gold RWT – Goldwin Rainwater Tank. All samples labelled soil are the sampled bioavailable Sr signal for the soil at depth of 35-50cm at each site.

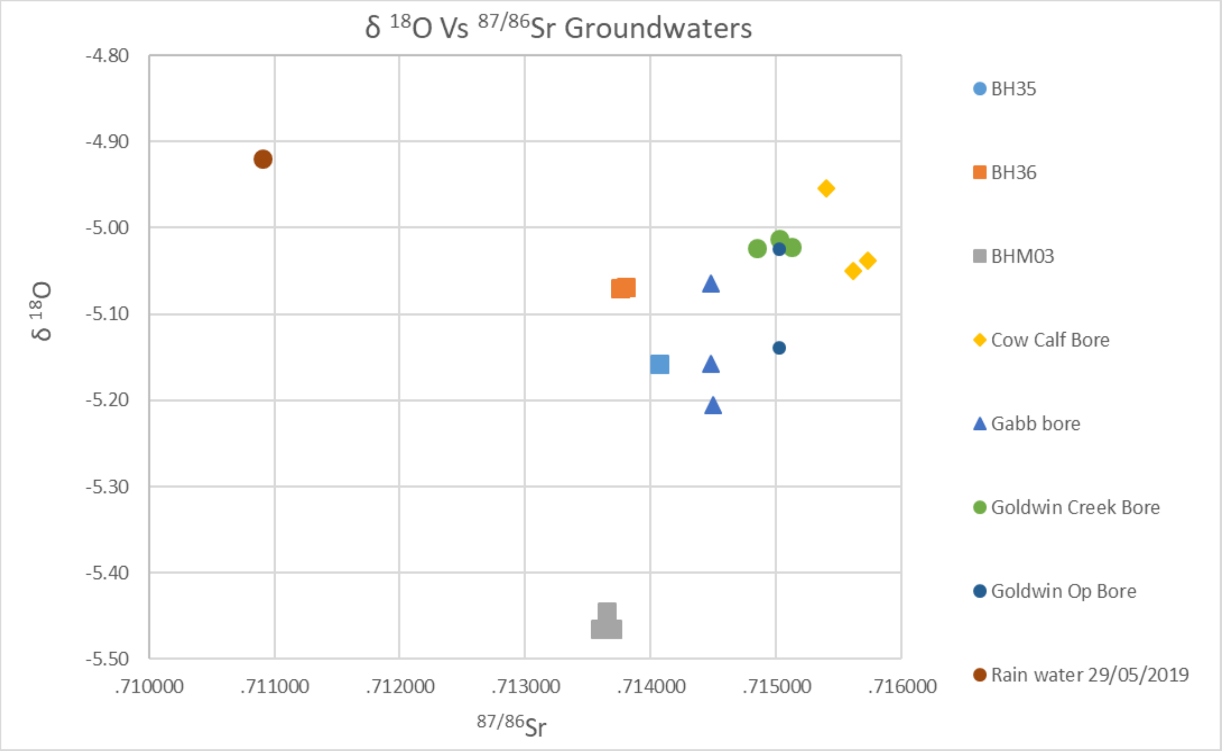


Figure 12: 18O against 87/86Sr signals for groundwater signals and rainwater. Shows a distinct groupings of BHMO3 and BH36, with greater variation in Sr and O amongst the shallower bores, particularly cowcalf and Gabb bore.

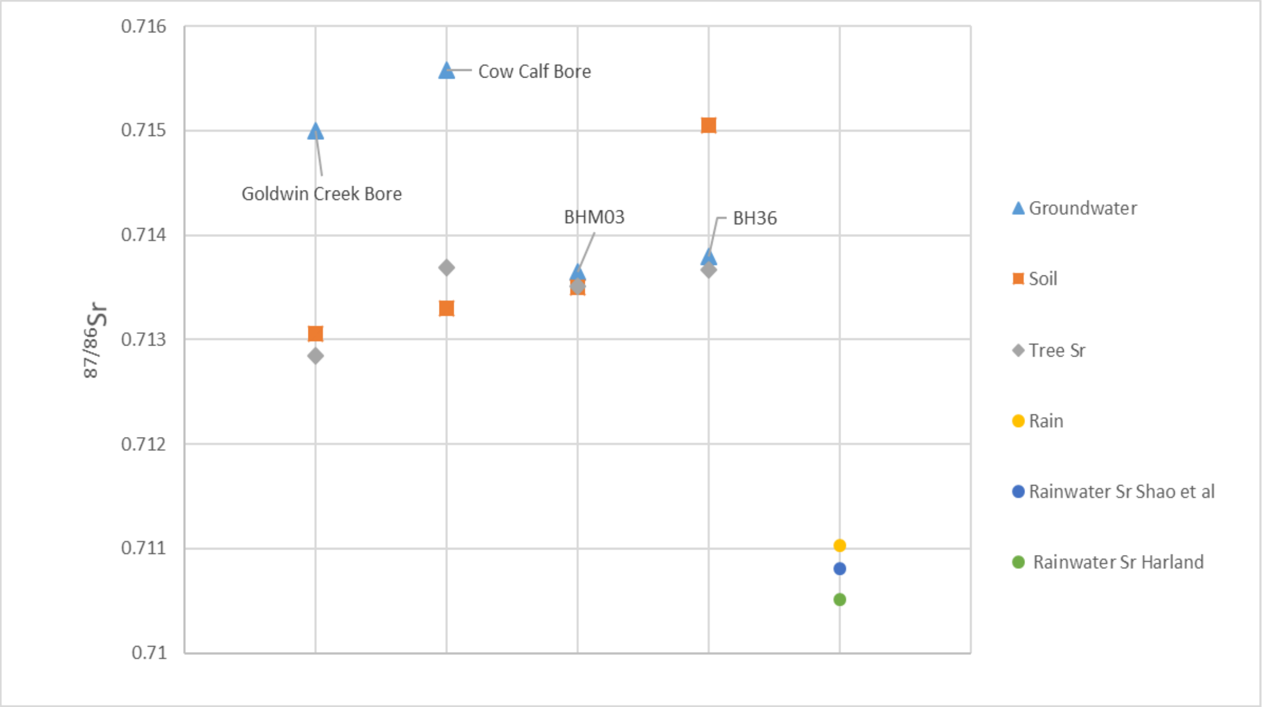


Figure 13: Comparison of each sample type at each site, with rainwater collected on site along with Adelaide rainwater from Shao et al. (2018) and Harland (2018). Note the clustering of BHMO3's Sr values for soil, tree and groundwater Sr, and the general trend of increasing bioavailable $^{87/86}$Sr with depth to groundwater for soil.

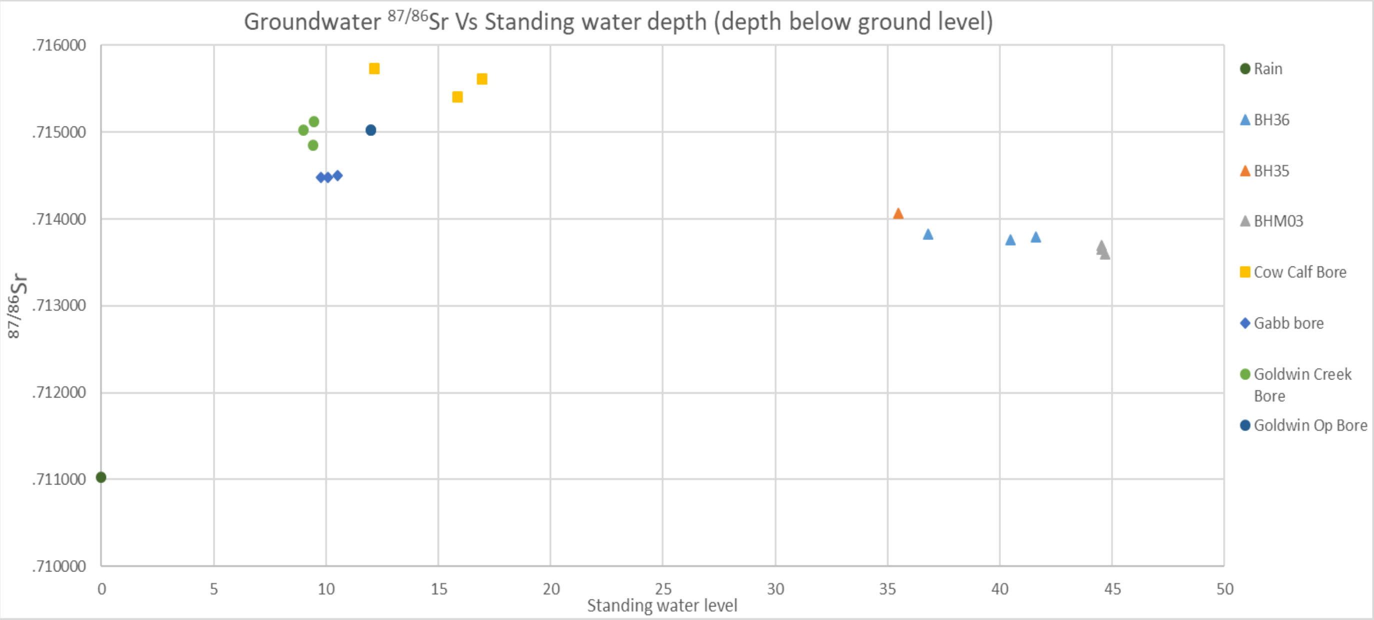


Figure 14: groundwater Sr values for observed sites against standing water level in meters.

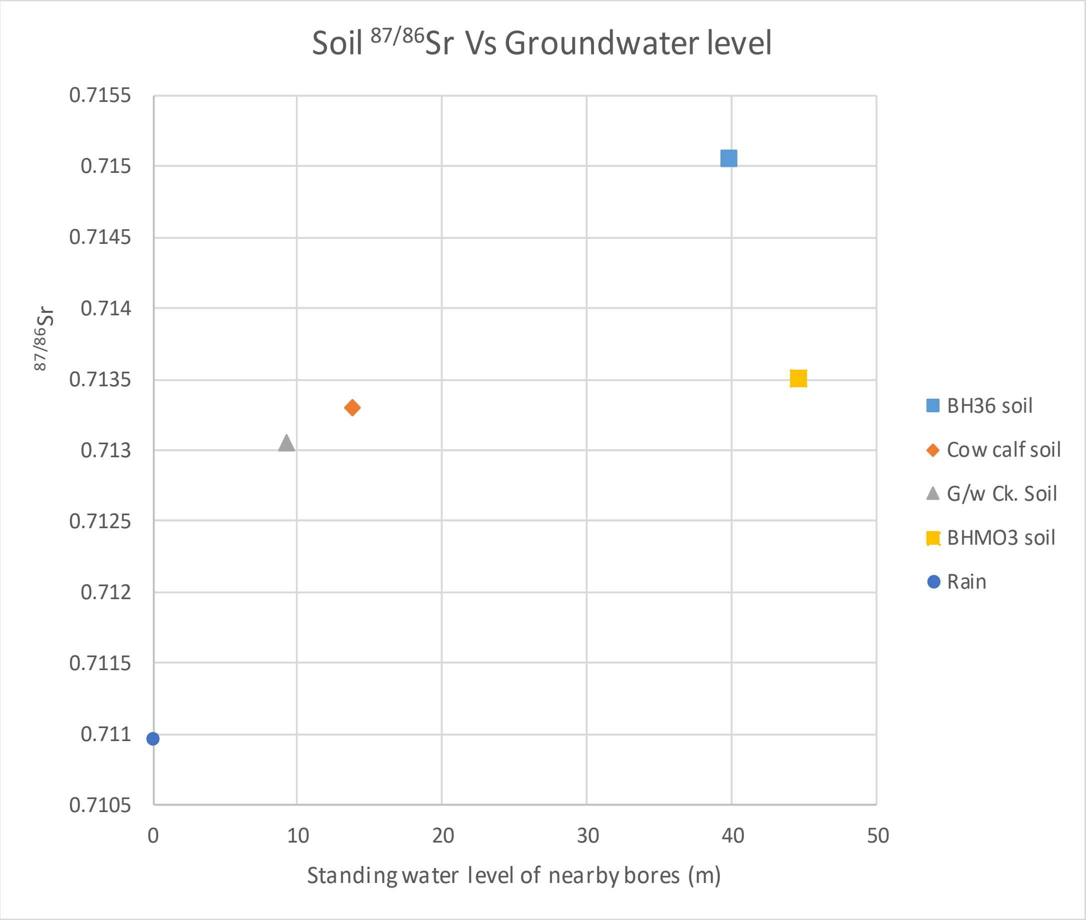


Figure 15: Soil Sr isotope values for observed sites compared to standing water level of nearby bores

DISCUSSION

$\delta\ ^{18}O$ and $\delta\ ^{2}H$

Groundwater across the BiH site showed a range of water isotope values over the sampling period and between sites. The groundwater signals are mostly clustered between the most enriched rainfall samples collected at the end of autumn and the most depleted samples collected at peak of winter. The groundwaters have higher $\delta\ ^{18}O$ than rainwater collected on site and from Mt Lofty ranges rainfall data from Guan (2009). This pattern is interpreted to reflect that the sampled groundwater sources represent the evaporated bulk rainfall supply to the region. The site's Mediterranean climate lends itself to yearly rainfall consisting mostly of isotopically depleted heavy winter rains and occasional, isotopically enriched summer rainfall events (Bestland et al., 2017; Guan et al., 2009; Guan et al., 2013). BHMO3 sits closest to the values of winter rainfall for δ D and $\delta\ ^{18}O$ and changes the least throughout the year. This suggests that BHMO3 is a slow recharging aquifer that is recharged mostly by winter rainfall that has experienced evaporation as it has moved through the upper strata. This aquifer is not impacted isotopically by smaller, less regular rainfall events in drier times. BH36 also shows less seasonal variation than the shallow bores, yet, potentially due to its more pronounced fracture system, does show some change from early autumn to late winter. Hence there is potential for large rainfall events to relatively rapidly reach the groundwater storage and impact the isotopic composition. The shallow aquifers accessed by Gabb , Cowcalf, Goldwin creek and Goldwin Op bores had a shift in isotope signatures for ^{18}O and Deuterium that was most significantly impacted by seasonal changes in the signature of rainwater. This suggests that the shallow and more quickly recharged bores represent a mix of evaporated bulk annual rainfall dominated by winter rains, but have their signal influenced when recharged by the most recent heavy rainfall event. This creates a situation where the groundwater isotopic signatures for the site are distinct from rainfall particularly towards the end of the drier months of the year, which is when the trees would be most reliant upon groundwater sources if they are accessible.

$^{87/86}$Sr ratios

All of the groundwater samples have Sr isotope signatures that are significantly different to that of rainwater, which shows that the groundwaters have the residence time to weather the surrounding rock/soil to the degree that the Sr ratios evolve away from the initial rainwater signature and towards that of the surrounding geology. There is a grouping of signals between the shallow and deep aquifers (Figure 14), indicating that there are differences in isotopic signal at different depths. This would occur if there is a change in rock type or mineralogy with depth, or that there are different weathering rates/solubility of Sr at different depths.

The strontium ratios from BHMO3, as can be seen in figures 11 and 13 are such that the soil, groundwater and leaf samples are well within error of each other. This suggests that the soil and the rock surrounding the groundwater aquifer come from the same bedrock source, without any change in strontium isotope signature (implying little to no change in base mineralogy) between the ground water storage, the soil layer that was sampled and the tree’s nutrient source, and that the trees access a nutrient source not isotopically impacted by atmospheric sources (Blum, Taliaferro, Weisse, & Holmes, 2000; Song, Ryu, Shin, & Lee, 2014). The BHMO3 drill log (Figure 6) shows that there is a PVC standpipe down the bore hole from 0-78m. The average SWL of 44.6m hardly varied across the sampling period, meaning that the water would have had to come up the pipe from > 78m. The BHMO3 drill core shows rock type geology that varies from sandstone to siltstone across the 100m of drill hole. The recharge rate of water entering the bore is quite low, and must reach the SWL from a depth > 78m. At this depth, the mineralogy and degree of weathering from water of the surrounding rock must be similar to that of the weathered sandy clay of the upper 2m. As there is no fractionation of Sr from the nutrient pool to the plant, the Eucalypts must access strontium from the deeper soil layers that are not influenced by atmospheric dust and rainfall inputs, as can be the case with more shallow rooted species (Hartman & Richards, 2014). The data from site BH36 was significantly different to BHMO3. At this site the soil strontium signal was the same for the tree core and groundwater samples, yet the soil sample was quite different, and much more ^{87}Sr enriched. This shows that the sampled Blue gums in this area source their nutrients from below the soil sample depth of 35-50cm, and that there is a distinct difference in the signature between the aquifer rock and the bioavailable Sr from the soil depth that was sampled. The bioavalible $^{87/86}$Sr for the soil is distinct from the groundwater, and even further from the atmospheric input from rain. It is difficult to determine why this is the case but this site is the main location for the old mine workings. Anecdotal reports suggest that there may have been soil and other material at the surface and at depth that are not from the immediate vicinity, transported as part of the mining processes of the late 1800s. This will require further investigation, but the Sr data does provide questions about the source water of the trees, or at least the depth of which the trees access soluble Sr sources. It has been shown that the tree's depth of uptake of Sr is below the surface layer and is accessing a soluble nutrient source that is of the same Sr value as the groundwater. The fracture system shown in the image from Aquaterra (Figure 5), shows bores around BH36 that have undergone geological investigation. Some fractures, particularly through BH24 are < 20m from the surface and are in known water bearing units, in a fracture system that is known to bear groundwater. BH36 also is the only one of the two deep bores sampled that shows a depleted water isotope signature towards winter rain. It is small, but it may indicate that this site has a more rapid recharge of rainwater than BHMO3, potentially as it has a greater fracture system closer to the surface that allows rainwater events to reach the groundwater storage. If the area around BH36 has water bearing fractures at < 20m like at BH24, then groundwater within the fractures and permeating into the soil may be well within the rooting range of local eucalypts. BH36 is in close proximity to the mine site and de-watering will occur in this area. It is likely that this location will experience the greatest draw down of water (Akker & Watson, 2017) and this should be taken into account prior to dewatering occurring.

All of the shallow bores sampled have a higher $^{87/86}$Sr signal than the deep bores sampled. This indicates that the waters are moving through different flow pathways to reach the shallow storage sites in the Goldwin Creek, Gabb property and Cowcalf locations, and that at the residence depths for these waters the mineralogy/weathering history of the storage zone is significantly different. There are also significant differences in signature between each of the sources sampled. The Goldwin Creek and Goldwin Creek Op. bores both access the same water source that is disconnected from the others. Cowcalf Bore had a strontium isotope signature most removed from rainwater, yet from the gathered data appears to be the most rapidly recharged from rain events. This indicates that the storage site for the groundwater accessed by Cowcalf bore is one with a surrounding material that is more radiogenic and potentially weathers higher Sr concentrations into the bore water than that of the other bores sampled. Goldwin Creek is similar, but not as exaggerated an example. Unlike at BHMO3, the soils around the shallow bores are much less radiogenic, and unlike at BH36, the tree samples for the shallow sites are more representative of the soils than the groundwater samples. This could be due to a combination of two main factors: the trees accessing two main soluble Sr sources at different times of year or under different rainfall conditions, and recycling of nutrients in the soil through litter fall (Poszwa et al., 2004). A hypothesis is put forward to explain this and is thus: the groundwater at each of these sites is well within rooting depth (Hubble, Docker, & Rutherfurd, 2010), and the tree species at these sites are *Eucalyptus camaldulensis*. This species' water requirements exceed those provided by rainfall alone and are met by the trees accessing groundwater (Doody, Holland, Benyon, & Jolly, 2009). As an adaptation to arid and semi-arid environments, it is opportunistic in its water use and hence it is unlikely that the trees do not access this groundwater to some degree. The standing water depth does not change greatly for Goldwin creek, and at the peak of summer Cow Calf bore (SWL 15.84m bgl) was still well within rooting depth for the sampled tree. In winter the trees access a mix of source water, mostly rainwater with a low concentration and depleted ^{87}Sr content. This Sr signature is stored in the leaves and wood. Rain also falls into the soil and contains the atmospheric input of Sr, with soluble cations making up the bioavailable fraction of atmospheric Sr and this lowers the surface soil and tree $^{87/86}$Sr. During the summer months or otherwise extended periods of drought soil water becomes much less available, and so the trees access a greater portion of their water from the groundwater

(Froend & Drake, 2006). Significant seasonal changes in water uptake depth of Australian phraeatophytic plants of dimorphic root morphology has been observed, particularly in Eucalyptus and Banksia species (Dawson & Pate, 1996). During the wet season (in this case, Autumn through to Spring) the trees acquire water mostly by uptake of recent precipitation from the upper soil layers, and tap roots derive water from the underlying ground water. As the dry season approaches, dependence on recent rain water is reduced while that on ground water increased. In high summer, shoots are well supplied with ground water taken up by the tap root. Thus plants are able to continue transpiration and carbon assimilation during the dry season. During the dry season plants derive the majority of the water from deeper sources while in the wet season most of the water is derived from surface sources upper soil layers (Dawson & Pate, 1996). Groundwater has a much greater concentration of Sr than rainfall, and as the roots are extracting water and nutrients from deeper in the soil, the Sr signal trends away from that of the atmospheric input. Over time this creates a long-term mix of Sr ratios stored in the tree, and the mix of signals gets recycled into the soil through litter fall nutrient cycling (see Figure 16 for a good conceptual overview of the bioavailable strontium fluxes for a forest system, from Poszwa et al. 2004). This creates an homogenised bioavailable signal in the soil and trees that represents a mix of high concentration, high $^{87/86}$Sr from tree litterfall (groundwaters do not reach the upper soil layers) and low Sr concentration, low $^{87/86}$Sr value from rainfall and throughfall, this homogenisation of bio-available soil Sr has been found in woodland forests with high litterfall before (Graustein & Armstrong, 1983). Much more sampling and investigation into Sr concentrations, differences in signal between the long term average from the wood core and the short term signal from the leaves, and seasonal variation in bioavailable strontium of the soils is necessary. This will provide the means to create a more reasonable argument for this hypothesis, as of now more work needs to be done over a longer time span.

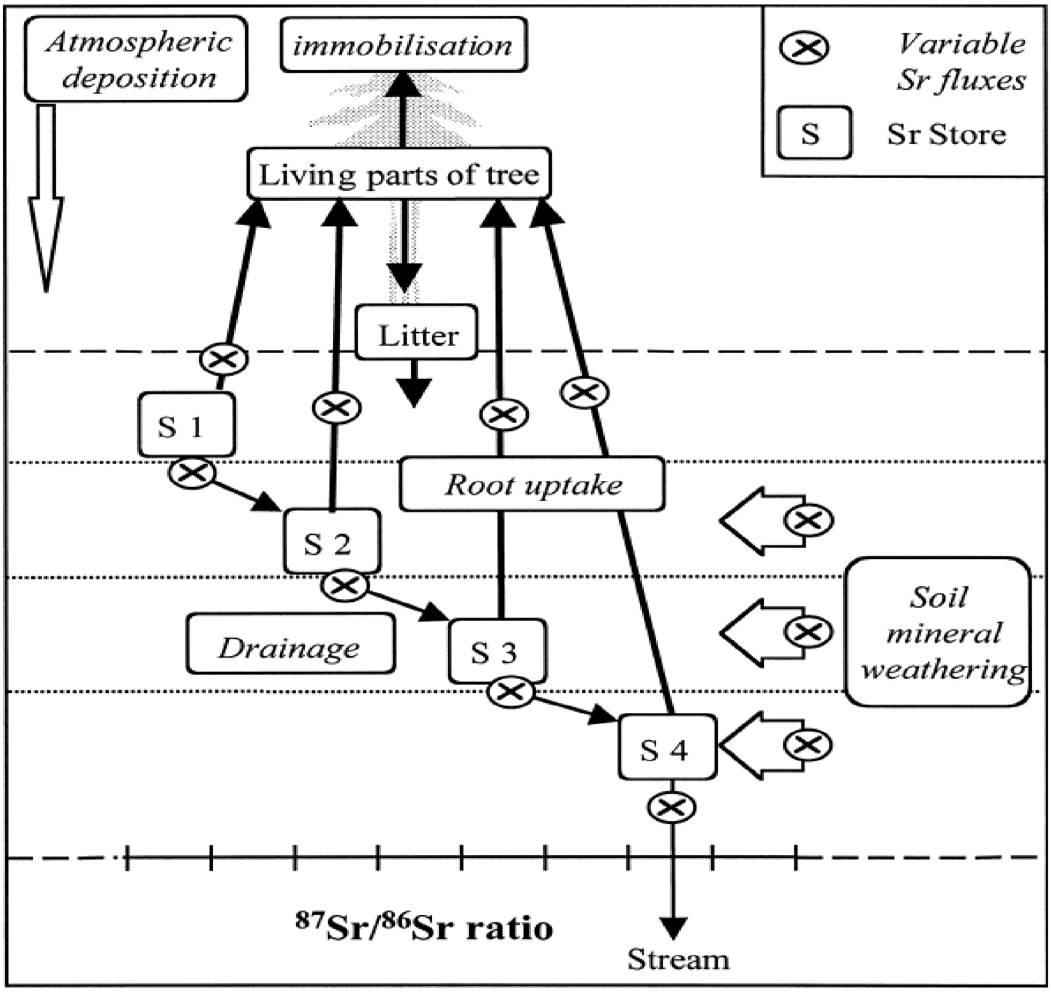


Figure 16: Conceptual diagram of Sr fluxes, storages and relative $^{87}Sr/^{86}Sr$ isotopic ratios in a boreal forest from Poszwa eta al. 2004. Note the sources of Sr: Atmospheric deposition, soil weathering and litter.

Opportunities for further study

It has been put forward that surface vegetation at several locations (BH36, Goldwin Creek, Cowcalf) are likely to have at least seasonal dependence on groundwater and therefore mining practices that lower the groundwater level may have an impact on the local ecology. The data shown here presents many opportunities for further study to be carried out in order to accurately determine the dependence of surface vegetation of the Bird in Hand NVHA on groundwater sources. It has been shown that the groundwater and rainwater isotopic signals are distinct and so future seasonally conducted sampling and isotopic analysis of Eucalypt xylem, rain and groundwater will be able to accurately determine seasonal source water of the keystone Eucalypts of the NVHA. Alongside further isotopic investigation, measuring of transpiration rates and sapwood area of eucalypts across the NVHA, to observe how water use changes for the trees over seasons. In areas where groundwater is not available, water use and transpiration will be significantly reduced during dry periods, while where there is access to groundwater and the trees are utilising it as a resource, the changes in water use patterns for the Eucalypts should not be as significant, or even not noticeably change at all (Doody et al., 2015; Feikema, Morris, & Connell, 2010).

These avenues of future study are what is required to truly determine the dependency of the NVHA on groundwater sources, and to what extent the system could be impacted as the dewatering process goes ahead. These investigations should be conducted over the course of the next two years prior to mine development and be taken into account when considering methods of mitigating potential impacts of the planned mine development.

CONCLUSIONS

The geochemical-hydrological study of the Bird-in-Hand mine NVHA area provided some useful insights into the hydrology and eco-hydrology of the region, and showed potential for further studies to provide answers to the key questions. The groundwater Sr data indicates that BH36 and BHMO3 bores draw groundwater from aquifers of similar mineralogy, yet the deuterium-oxygen data shows that they have significantly different hydrological patterns and are most likely disconnected systems. The shallow groundwater sites display similar hydrological patterns to each other in terms of the way rainfall events infiltrate the storage zone through the alluvial layer, yet they show a range of different Sr values, showing geographical shifts in the mineralogy and/or weathering history of the groundwater storages. Although these bores access groundwater of similar depths and structures, the available data suggests these bores are disconnected from each other hydrologically. Differing recharge pathways could explain the differences in water isotope composition of the sampled groundwaters, with the more evaporated (shallower or more fractured) aquifers being recharged from rainfall moving through the unsaturated surface layers into the groundwater storages. BHMO3 may be recharged by deep, slow moving waters that store a long term, bulk signal of rainfall, sourced from indirect, localised or non-localised recharge sources. More investigation and tracing of the isotopic signature of the water moving from the surface into the groundwater storages is necessary to build a better understanding of the individual recharge pathways of these aquifers. The data further suggests that the sampled bores will retain an O and D signature that is removed from that of rain and surface soil waters, and hence analysis of these recharge pathways and of the source water of local Eucalypt species is possible across the site using isotope analysis methods. The Eucalypt trees at the shallow bore sites appear to access a mixture of groundwater and rainwater, while fracture zones around BH36 may provide groundwater access to deep-rooted trees in the area. Future sampling of several soil layers at each site, of groundwaters, as well as rain and tree stems should be conducted at a minimum seasonally to identify seasonal changes in signal for rainfall, soil, groundwater and plant isotopes.

A refined, cryogenic vacuum distillation method with suitable equipment and consideration of potential issues with this method should be applied to effectively extract water from the stem and soil samples, along with direct monitoring of tree water use and transpiration. Analysis should then be conducted, and it will be possible to determine the source water for the keystone *Eucalyptu*s species of the NVHA. For further isotopic-hydrological investigations to be effective a yearlong or bi-annual study period will be required in order to truly understand the hydrology and ecohydrology of the area and the influence of the seasons.

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