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A 35 ka record of groundwater recharge in south-west Australia using stable water isotopes

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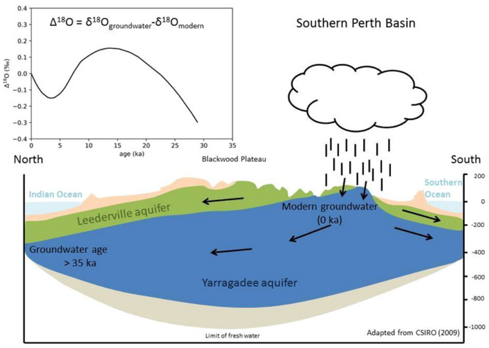
HIGHLIGHTS

- Perth Basin groundwater isotope record is a low-resolution archive of recharge.
- Modern groundwater recharge is biased to high volume/high intensity rainfall.
- Palaeo-recharge varies due to recharge thresholds and relative volume of rainfall.

GRAPHICAL ABSTRACT



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ABSTRACT

The isotopic composition of groundwater can be a useful indicator of recharge conditions and may be used as an archive to infer past climate variability. Groundwater from two largely confined aquifers in south-west Australia, recharged at the northernmost extent of the westerly wind belt, can help constrain the palaeoclimate record in this region. We demonstrate that radiocarbon age measurements of dissolved inorganic carbon are appropriate for dating groundwater from the Leederville aquifer and Yarragadee aquifer within the Perth Basin. Variations in groundwater $\delta^{18}O$ values with mean residence time were examined using regional and flow line data sets, which were compared. The trends in the regional groundwater data are consistent with the groundwater flow line data supporting the hypothesis that groundwater $\delta^{18}O$ is a robust proxy for palaeo-recharge in the Perth Basin. A comparison between modern groundwater and rainfall water isotopes indicates that recharge is biased to months with high volume and/or intense rainfall from the westerly wind circulation and that this has been the case for the last 35 ka. Lower stable water isotope values are interpreted to represent recharge from higher volume and/or more intense rainfall from 35 ka through the Last Glacial Maximum period although potentially modulated by changes in recharge thresholds. The Southern Perth Basin groundwater isotopic record also indicates a trend towards higher volume and/or intense rainfall during the Mid- to Late Holocene. The long-term stable water isotope record provides an understanding of groundwater palaeo-recharge. Knowledge of recharge dynamics over long time scales can be used to improve current water sharing plans and future groundwater model predictions.

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1. Introduction

South-west Australia's location at the northernmost extent of the Southern Hemisphere westerly wind belt makes it sensitive to past, and future, climate change. In this region, a consensus on climate drivers, rainfall variability, and groundwater recharge since the Last Glacial Maximum (LGM, ~22–18 ka; Petherick et al., 2013) is lacking. Groundwater can be a useful archive of rainfall isotopic composition, which, in turn, can help to understand the drivers and impacts of rainfall and climate changes (Haldorsen et al., 2016; Rozanski et al., 1997). Furthermore, an understanding of the relationship between climate and groundwater recharge in the past can be used to inform climate adaptation strategies for managing groundwater resources during climate change and thus improve 'sustainable' use of current groundwater resources. This is especially critical for groundwater systems that were recharged prior to the Holocene (before 11.7 ka), in locations where groundwater extraction often exceeds modern groundwater recharge. Until recently a lack of groundwater observations has limited our understanding of the dynamic relationship between groundwater recharge and climate (Taylor et al., 2012).

A number of factors can determine the long-term fluctuations of the stable water isotope composition of rainfall including: temperature, air mass origin, humidity, moisture recycling and ice volume (Rozanski et al., 1997). In former glaciated areas of North America and North Europe the difference between the LGM climatic conditions and those of modern or Late Holocene are dramatic as groundwaters show definite hydrogeochemical changes that can be linked to climate. For example, ^{18}O-depleted groundwater with δ^{18}O values at least 1‰ lower than Holocene that originated from glacial melt has been encountered in Europe and Canada (Hendry et al., 2013; Jiráková et al., 2011; Raidla et al., 2019).

In the absence of glaciation, the groundwater stable water isotope composition generally reflects the weighted mean isotopic composition of the rainfall in the recharge area (Rozanski et al., 1997), although dispersion and/or water–rock interactions within the aquifer can make groundwater difficult to interpret for palaeo-recharge conditions. Nevertheless, in systems which are not dominated by in situ processes, groundwater archives serve as low-resolution (centennial- to millennial-scale) palaeoclimate records and can offer valuable insights to climatic changes worldwide (Haldorsen et al., 2016). Moreover, the groundwater palaeo-recharge record may be one of the simplest ways of getting long, although low-resolution, palaeo-records. Many groundwater systems throughout Australia were recharged during previous climatic periods (for example, Cartwright et al., 2012; Harrington et al., 2013; Love et al., 1994; Meredith et al., 2018), hence the groundwater isotopic records contained in regional aquifer systems may be an archive of past hydrological and climatic changes (Edmunds, 2005; Rozanski et al., 1997).

This research will focus on a large regional aquifer system, the Perth Basin, which is located in south-west Australia. The Perth Basin aquifers contain large volumes of groundwater that support ecosystems and an ever increasing demand for irrigation and potable water supply for south-west Australia (Barron et al., 2012). Because of the importance of this groundwater resource there have been a considerable number of groundwater investigations undertaken (for example, AECOM, 2015; Department of Water, 2017a; Meredith et al., 2012a), as well as studies on the potential impact of future climate change (Ali et al., 2012; Barron et al., 2012; McFarlane et al., 2012). The majority of groundwater studies in the Perth Basin involved the collection of hydrogeochemical data, including radiocarbon ($^{14}C_{DIC}$) and stable oxygen and hydrogen isotope values (δ^{18}O and δ^{2}H) in water. The objective of this project is to use the datasets generated from two largely confined aquifers within the Perth Basin to understand recharge conditions and past climate for south-west Australia over the past ~35 ka. Regional scale databases containing mean residence time and isotopic records are not commonly available in Australia, or internationally, and are generally more site specific. Therefore, this database with over 300 radiocarbon age measurements for the Perth Basin forms a unique low-resolution palaeo-archive of groundwater recharge conditions for south-west Australia. Gaining an understanding of south-west Australia groundwater recharge and linking this to palaeoclimate may improve climate model predictions of future climate and groundwater recharge (Barron et al., 2012; Gouramanis et al., 2012)

2. Study area

The Leederville aquifer and the Yarragadee aquifer within the onshore portion of the Perth Basin are the focus of this research. The onshore Perth Basin is a half-graben basin with Permian to Cretaceous sediments deposited in a rift system that culminated with the breakup of Gondwana in the Early Cretaceous (Department of Mines and Petroleum, 2014). It covers approximately 45,000 km^2 of Western Australia, and is 30 to 100 km wide and 1000 km long reaching from Geraldton along the western coastline to the south-west corner of Western Australia (Fig. 1 inset; CSIRO 2009; Department of Mines and Petroleum, 2014). The area is comprised of the coastal plains with elevations below 150 m AHD along the coastal region throughout the majority of the basin, and escarpments along the western margin of the Perth Basin with an average elevation of about 350 m AHD (CSIRO, 2009). Smaller plateaus of uplifted sedimentary rocks occur in the north-east and southern portion of the Perth Basin. Almost all rivers originate on the plateau bordering the eastern margin of the basin before entering the flatter coastal plains.

The region has a Mediterranean-type climate with distinct hot dry summers and cool wet winters. Mean annual maximum and minimum daily temperatures are 25.9°C and 13.6°C, respectively with mean maximum daily temperature in summer of 31.3°C and mean minimum daily temperature in winter of 9.7°C (Bureau of Meterology 2019). A subtropical belt of high pressure which extends across the region in summer migrates northward during autumn and lies almost entirely north of the region during winter (Bates et al., 2008; Hope et al., 2006). Approximately 80% of meteoric precipitation falls between April and October when the circumpolar vortex of westerly winds carrying southern maritime air masses shift northwards due to the positioning of the subtropical high pressure belt to the north (Bates et al., 2008; Sturman and Tapper, 2006). Although infrequent, summer rainfall from thunderstorms and ex-tropical cyclones can produce significant event-based rainfall. There is a strong rainfall gradient from south-west to north-east with average annual rainfall decreasing from approximately 1000 mm in the south-west coastal parts of the Perth Basin to <350 mm in the north-east as the mean depression track is always south of the region (Bates et al., 2008; Hope et al., 2006).

2.1. Hydrogeology

The onshore Perth Basin is composed of a number of groundwater areas, however the aquifers are divided into the Northern Perth Basin flow system, which extends from Geraldton to Three Springs; Central Perth Basin flow system that incorporates the Peel-Harvey flow system (CSIRO, 2009), which extends from Moora to Binningup, and Southern Perth Basin flow system which extends from Binningup to the south coast (Fig. 1).

The Perth Basin is highly developed, with ~850 GL of groundwater used annually for agriculture, industry, mining and household

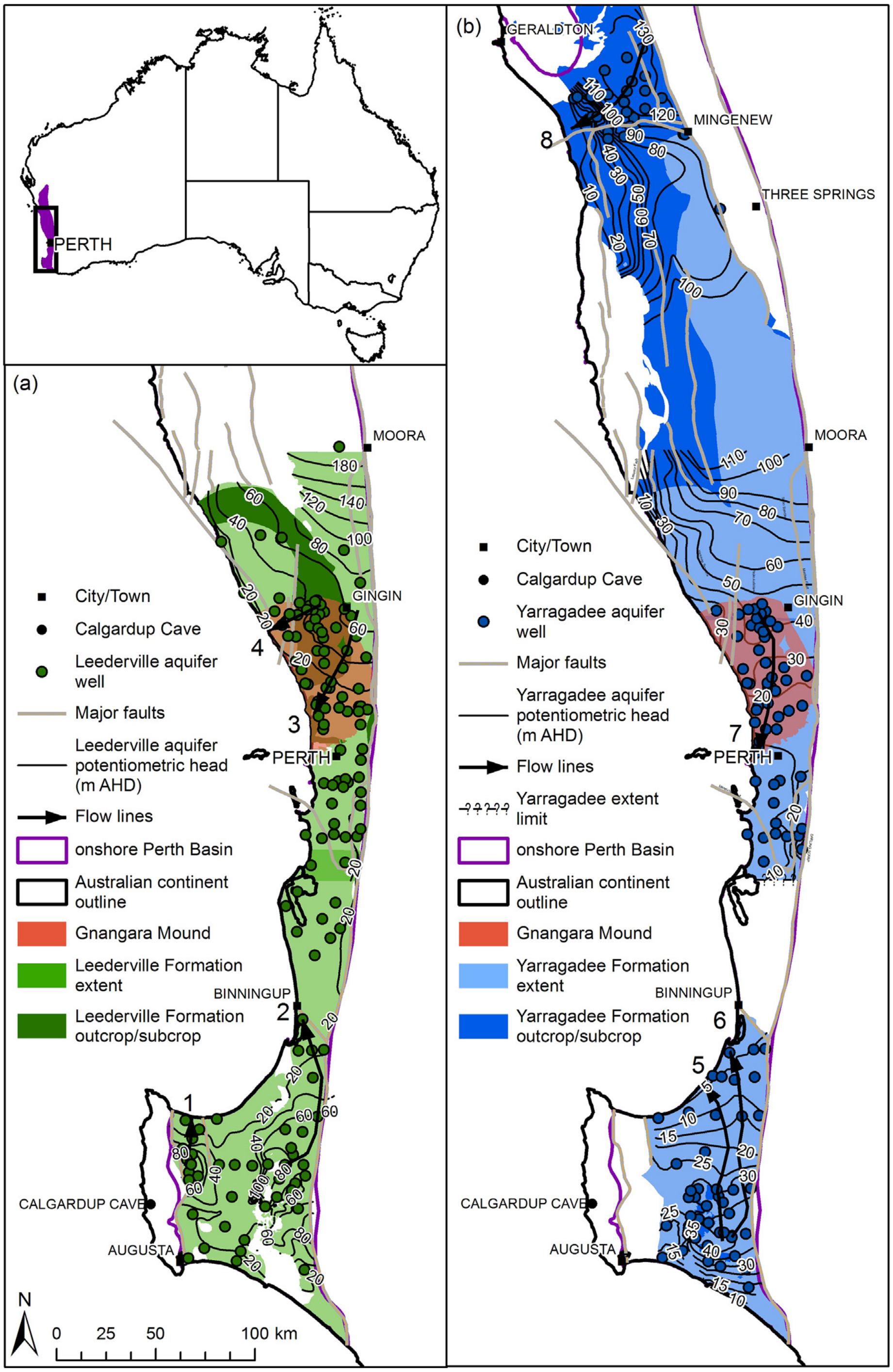

Fig. 1. (inset) Onshore Perth Basin location. Cased well location, aquifer extent and (sub)crop out locations for (a) Leederville aquifer and (b) Yarragadee aquifer collated from AECOM, (2015); Department of Water, (2017a, 2017b); EGIS E.G.I.S. Consulting, (1999); Harrington et al., (2015); Kern and Koomberi, (2010); Leaney, (2004); Meredith et al., (2010, 2012a, 2012b); Schafer et al., (2008); Thorpe, (1992); Thorpe and Baddock, (1994); Thorpe and Davidson, (1990); Turner and Dighton, (2008). Major fault locations and generalised groundwater flow direction adapted from Baddock et al., (2005); Davidson and Yu, (2006) and Department of Water, (2017b). Numbers along the coastline represent the flow line number.

water supply (CSIRO, 2009). The three main aquifers used are: the Superficial aquifer, and the generally confined Leederville and Yarragadee aquifers that are the focus of this study. The hydrogeology of these aquifers is discussed below and a simplified stratigraphic sequence for the Northern Perth Basin, Central Perth Basin and Southern Perth Basin is given in Supplementary Material Table S1; however for a comprehensive review of the geology and hydrogeology of the onshore Perth Basin the reader is referred to CSIRO, (2009) and Department of Mines and Petroleum, (2014).

The Superficial aquifer is a multi-layered unconfined aquifer system consisting of Cenozoic sequences of sand, limestone, silt and clay. The stratigraphy and lithology of the deposits varies across the basin with sand and limestone deposits occurring at the coast, and throughout the Central Perth Basin and Southern Perth Basin; and alluvial, clayey and sandy aeolian deposits extending over the Northern Perth Basin (CSIRO, 2009). Recharge to the Superficial aquifer predominantly occurs by rainfall infiltration with rates depending on rainfall, watertable depth, lithology, topography and land cover. Some recharge to the Superficial aquifer also occurs through upward leakage from underlying formations. Discharge is to the ocean, artificial and natural drainage systems and coastal lakes. Losses also occur from wetlands and in areas with a shallow watertable by evaporation, and increasingly from abstraction of water (up to 85% (414 GL) in 2007 of groundwater use throughout the Central Perth Basin; CSIRO, 2009); thus samples from the Superficial aquifer were not included in this palaeo-recharge study.

The Leederville aquifer is a multi-layered generally confined aquifer in the Central Perth Basin and Southern Perth Basin which consists of discontinuous interbedded sandstone, siltstone and shale deposited during the Early Cretaceous Epoch. The Leederville aquifer is confined by overlying Kardinya Shale Member of the Osborne Formation in the north, as well as locally by the discontinuous interbeds of siltstone, shale and clay within the Leederville Formation. It is about 600 m thick in the Central Perth Basin, and between 50 and 300 m thick in the Southern Perth Basin, with horizontal hydraulic conductivities for the sandstone layers up to 10 m/day (CSIRO, 2009; Davidson and Yu, 2006). It is absent where the Yarragadee Formation subcrop the superficial formations throughout most of the Northern Perth Basin, north of Moora (Fig. 1a), and at various locations along the Central Perth Basin and Southern Perth Basin (Fig. 1a; CSIRO, 2009; Strategen, 2004). The Leederville aquifer becomes unconfined where it (sub)crops below the Superficial aquifer west and north-west of Gingin (Fig. 1a; CSIRO, 2009; Strategen, 2004). Recharge occurs from overlying aquifers where confining beds are absent, such as through the Gnangara Mound, west of Gingin, and Southern Perth Basin via rainfall infiltration in outcrop areas (Fig. 1; Davidson and Yu, 2006; Meredith et al., 2012b), and direct infiltration into the Leederville aquifer occurs in deep valleys between Moora and Gingin (CSIRO, 2009; Davidson and Yu, 2006). Groundwater flows are generally from the north-east to the south-west in the Central Perth Basin, and from preferential recharge areas, such as within the Southern Perth Basin, with offshore discharge to the ocean through the Superficial aquifer (Fig. 1a). Additionally, where the South Perth Shale is absent and the hydraulic gradients are downward groundwater has the potential to leak into the underlying Yarragadee aquifer (Davidson and Yu, 2006).

The Yarragadee aquifer is a deep multi-layered generally confined aquifer comprised of sandstone with minor shale horizons which were deposited during the Middle to Late Jurassic Epoch. In most areas across the Perth Basin, the Leederville Formation overlies the Yarragadee aquifer and the Yarragadee aquifer is confined by the overlying South Perth Shale, the Otorowiri Member of the Parmelia Formation (Northern Perth Basin) or shale beds of the lower part of the Leederville Formation (Southern Perth Basin; CSIRO, 2009). The Yarragadee Formation is >2000 m thick and is the most widespread formation in the Perth Basin with horizontal hydraulic conductivities for the sandstone layers up to 10 m/day (CSIRO, 2009; Davidson and Yu, 2006). The Yarragadee aquifer is unconfined where it (sub)crops out in the Northern Perth Basin and in the Southern Perth Basin (Fig. 1b; CSIRO, 2009). Recharge via rainfall occurs where the aquifer crops out, as well as downward leakage where the aquifer subcrops the Superficial aquifer and Leederville Formation. Groundwater flows are generally from the north/north-east to the west/south-west in the Northern Perth Basin and Central Perth Basin, and from preferential recharge areas in the Southern Perth Basin (Fig. 1b). The majority of groundwater flow is assumed to occur in the upper 500 m with most discharge offshore or via upward leakage into overlying aquifers where the aquifers are in contact and there is an upward gradient (CSIRO, 2009; Department of Water, 2017b).

There are a number of faults identified throughout the area (Fig. 1); however, most in the Central Perth Basin appear to allow lateral, rather than vertical leakage between the Superficial aquifer, Leederville aquifer and Yarragadee aquifer (Department of Water, 2017a). In the Northern Perth Basin faults may be acting as conduits for saline groundwater flow and may make the Yarragadee aquifer locally discontinuous (Fig. 1; Meredith et al., 2012a; CSIRO, 2009). In addition to lateral connectivity across faults, systematic groundwater abstraction since 1962 may be altering the natural flow direction in these well fields causing anthropogenic mixing within the aquifers (CSIRO, 2009; Davidson and Yu, 2006). Abstraction is non-uniform due to demand and variable in extent, depth and salinity of the aquifers. The Central Perth Basin has the highest use with an estimated 61 GL and 60 GL extracted from the Leederville aquifer and Yarragadee aquifer, respectively, in the Perth Region in 2004 (CSIRO, 2009; Davidson and Yu, 2006).

3. Material and methods

3.1. Data collection

Hydrogeological and groundwater geochemistry data for the Leederville aquifer and Yarragadee aquifer were collated from the following published government reports and journal articles including: AECOM, (2015); Department of Water, (2017a, 2017b); EGIS E.G.I.S. Consulting, (1999); Harrington et al., (2015); Kern and Koomberi, (2010); Leaney, (2004); Meredith et al., (2010, 2012a, 2012b); Schafer et al., (2008); Thorpe, 1(992); Thorpe and Baddock, (1994); Thorpe and Davidson, (1990); Turner and Dighton, (2008). Where geochemistry data has been duplicated in the literature both sources are referenced. The Department of Water and Environmental Regulation Water Information Reporting database was used to collate additional location, hydrogeological and geochemistry data when omitted from the published literature.

A total of 376 groundwater geochemical samples sampled between 1992 and 2016 were collated from the literature. Of these 38, 212 and 126 samples were from the Northern Perth Basin, Central Perth Basin and Southern Perth Basin, respectively; with 127 and 66 being from the Leederville aquifer in the Central and Southern Perth Basin, respectively.

Aquifer extent, (sub)crop out and fault locations, as well as groundwater flow directions were collated for the Leederville aquifer and Yarragadee aquifer from Baddock et al., (2005); Davidson and Yu, (2006) and Department of Water, (2017b). Flow lines (Fig. 1) were interpreted using the published groundwater flow directions where there were 6 or more wells with geochemistry data.

3.2. Quality control

A number of measures were undertaken to assure the data collated and used are representative and accurate. Firstly, only results for wells with ^{14}C and δ^{13}C of dissolved inorganic carbon (DIC), as well as δ^{18}O, δ^{2}H, alkalinity, pH and major ions (Cl, Br, SO_4, Ca, K, Mg and Na) analysis results were collated, with the following exception. Well samples that did not have all of these analysis results associated with them but provided duplicate measurements of ^{14}C, δ^{13}C, δ^{18}O or δ^{2}H were included to permit the reproducibility of the results to be verified. Secondly, the hydrogeological and geochemistry data collated from the published literature were compared to the original well reports in the Department of Water and Environmental Regulation Water Information Reporting database to ensure the hydrogeological data presented is correct. Thirdly, to ensure that the data is representative of the sampled aquifers, those samples with evidence of evaporation, mixing with surface water/groundwater sourced from other aquifers or alteration due to pumping have been removed from the dataset. These processes, described briefly in section 2.1, have been identified for a number of samples in the published literature, and confirmed here by increased $\delta^{18}O$ and $\delta^{2}H$ values due to evaporation, increased chloride concentrations, as well as variation of $^{14}C_{DIC}$ content along groundwater flow lines and with sampling depth, as outlined in detail in the Supplementary Material section A1. Finally, those samples with measured $^{14}C_{DIC}$ values <1 pMC (normalised percent modern carbon; Plummer and Glynn, 2013) were excluded from radiocarbon dating as these measurements are within analytical error. Details on the quality control procedures are provided in the Supplementary Material. The complete dataset is provided in Supplementary Electronic data file 1 with any of the identified issues or processes noted. The final dataset utilised for this study is presented in Supplementary Electronic data file 2.

3.3. Radiocarbon dating

Radiocarbon dating of DIC in groundwater is the most accessible and widely used technique to date groundwater resources up to ~40 ka (Plummer and Glynn, 2013). The groundwater residence time is calculated by:

$$t = -\frac{t_{1/2}}{ln2} ln \frac{14C_m}{14C_0} \quad (1)$$

where t is the conventional radiocarbon age and is expressed in years before present (BP) where present is the year 1950, $^{14}C_m$ and $^{14}C_0$ are the measured and initial $^{14}C_{DIC}$, and $t_{1/2}$ = 5,568 years, the Libby half-life (Münnich, 1957; Plummer and Glynn, 2013). Geochemical adjustment models can be used to estimate $^{14}C_0$ by correcting for geochemical reactions that occur along a groundwater flow path which affect DIC and dilutes the $^{14}C_{DIC}$ concentration by the addition of 'dead' carbon which is independent of the radioactive decay of $^{14}C_{DIC}$ (Kalin, 2000; Plummer and Glynn, 2013). DIC (sum of CO_2 + HCO_3^- + CO_3^{-2} in solution) of the groundwater samples for radiocarbon dating was calculated from the alkalinity and pH using a PHREEQC aqueous speciation model. The interpretation of the corrected radiocarbon age is the $^{14}C_{DIC}$ piston flow age calculated by a geochemical adjustment model applied to DIC (Plummer and Glynn, 2013). In addition to the geochemical reactions that affect DIC, radiocarbon dating should be undertaken on the denormalised pmc values, rather than normalised pMC values (Mook and van der Plicht, 1999; Plummer and Glynn, 2013). However, insufficient information was included in the literature to denormalise the reported pMC values; therefore, the calculated radiocarbon ages include a relatively small error from the use of pMC, rather than pmc values (Plummer and Glynn, 2013).

Conventional (uncorrected) radiocarbon ages are calculated considering only decay and assuming $^{14}C_0$ = 100 pMC (Plummer and Glynn, 2013). To account for geochemical reactions that occur along a groundwater flow path, the Pearson's model and Han and Plummer's model have been used. The Pearson geochemical adjustment model constructs an isotope mass balance to account for the simple process of dissolution of carbonate by dissolved soil CO_2 under closed-system conditions, and the resulting $^{14}C_{DIC}$ dilution (Ingerson and Pearson, 1964; Plummer and Glynn, 2013). Han and Plummer's model is a combination of three models (the Tamers' model, Mook's model and Eichinger's model) and accounts for both carbon isotopic exchange dominated by gaseous CO_2 in the unsaturated zone, and for carbon isotopic exchange dominated by solid carbonate mineral in the saturated zone (Han and Plummer, 2013; Han and Plummer, 2016). The radiocarbon ages calculated from Han and Plummer's model can be biased to younger ages, whereas the radiocarbon ages calculated by the Pearson model may be biased to older ages (Han and Plummer, 2016).

To compare radiocarbon mean residence times with palaeohydrological information from terrestrial records the radiocarbon ages of groundwater were calibrated to calendar years before present using a calibration curve (Bard et al., 1998; Kitagawa and van der Plicht, 1998; Plummer et al., 2004; Reimer et al., 2004; Stuiver et al., 1998). A radiocarbon calibration is needed because the ^{14}C content of atmospheric CO_2 has varied in the past and the conversion to calendar years before present refinement for hydrologic systems provides more accurate estimates of calendar ages (Fairbanks et al., 2005; Plummer and Glynn, 2013; Stuiver et al., 1998).

3.4. Water isotopic data

To aid in the visualisation of $\delta^{18}O$ trends over time, the water isotope data was 'smoothed' to a LOESS curve using a LOESS nonparametric regression method (Cleveland et al., 1992). A quadratic function was fitted with a span of 0.75 to capture the $\delta^{18}O$ trend within the data but avoid overfitting a large variance curve. The regional $\delta^{18}O$ trends over time were then compared to $\delta^{18}O$ trends for interpreted flow line derived data in order to verify that the regional $\delta^{18}O$ trend in Perth Basin dataset are an isotopic archive of past variability in groundwater recharge.

To assist in the interpretation of the drivers of groundwater isotopic values during the Late Pleistocene, the groundwater $\delta^{18}O$ values are compared to the isotopic effect of increased glacial ice and reduced temperatures. Increased glacial ice changes the isotopic values in seawater and rainfall due to enhanced storage of the lighter isotopes in glacial ice (Bintanja and Wal, 2008) and reduced global temperatures impact on rainfall $\delta^{18}O$ (Dansgaard, 1964). This is done by normalising the groundwater $\delta^{18}O$ LOESS curve by the modern values producing groundwater $\Delta^{18}O$ relative to modern values ($\Delta^{18}O = \delta^{18}O_{groundwater} - \delta^{18}O_{modern}$). The ice sheet contribution to the marine isotope signal relative to present ($\Delta^{18}O_{ice\text{-}vol}$) and the impact of a cooler atmosphere on rainfall $\delta^{18}O$ ($\Delta^{18}O_T$) was calculated following the method used by Treble et al., (2017). Briefly, the ice sheet contribution to the marine isotope reconstruction from Bintanja and Wal, (2008) was used to scale $\Delta^{18}O_{ice\text{-}vol}$. Also, an estimate of $\Delta^{18}O_T$ range was calculated by using a sea-surface temperature record for the Southern Ocean (36°44′S, 136°33′E) reconstructed by Calvo et al., (2007) and for the Southern Pacific Ocean (40°23′S, 177° 59′E) reconstructed by Pahnke and Sachs, (2006), and applying this to the O isotope fractionation of Horita and Wesolowski, (1994). The corrected $\delta^{18}O$ values were used to estimate groundwater $\delta^{18}O$ values accounting for the isotopic effect of increased glacial ice and reduced temperatures.

Rainfall $\delta^{18}O$ and $\delta^{2}H$ measurements have been collected in Perth, within the Perth Basin, as part of the Global Network of Isotopes in Precipitation (Hollins et al., 2018), and from above Calgardup Caves located approximately 10 km from the Perth Basin boundary (Fig. 1). The amount weighted mean summer (December–February), winter (June–August) and annual rainfall for Perth were calculated using monthly data from 1962 to 2014 (n = 348) in Hollins et al., (2018) and for Calgardup Caves using data from 2006 to 2018 (n = 156) in Griffiths et al., (Unpublished results). The proximity of these rainfall collection sites to the Perth Basin means the continental rainout effect on rainfall $\delta^{18}O$ and $\delta^{2}H$ would be inconsequential over this distance (Hollins et al., 2018).

4. Results and discussion

4.1. Radiocarbon values of groundwaters in the Perth Basin

Groundwater $^{14}C_{DIC}$ values vary with depth and distance along groundwater flow paths. A number of criteria were applied to the data to determine if $^{14}C_{DIC}$ piston flow mean residence times could be calculated for the dataset (Supplementary Material section A2). The piston flow assumption holds for the majority of the data in the Southern Perth Basin (only 6 of 126 samples were excluded; Supplementary Material) with $^{14}C_{DIC}$ values in the Leederville aquifer and Yarragadee aquifer in agreement with groundwater flow trends. This trend is not observed in the Northern Perth Basin where modification of $^{14}C_{DIC}$ values along the flow path due to fault induced groundwater mixing with saline groundwater has been identified in several samples toward the start of the inferred flow line (9 of 38 samples; Supplementary Material; Meredith et al., 2012a). The remaining Northern Perth Basin samples show no evidence of mixing being located further away from the fault responsible, and having met all other quality control measures outlined in the Supplementary Materials, have been retained in this dataset. Likewise, in the Central Perth Basin a number of samples (11 of 212 samples; Supplementary Material) were removed from the dataset due to there being evidence of mixing with younger and older groundwater. Groundwater abstraction may be causing alteration of the natural groundwater flow in this part of the Perth Basin (Davidson and Yu, 2006); however, all samples that met the quality control measures have been retained in the study to assess whether there is a climate signal evident in the groundwater.

In addition to physical flow processes, it was considered whether chemical processes such as carbonate dissolution could impact the $^{14}C_{DIC}$ value. DIC concentrations are generally low throughout the Perth Basin (average DIC = 3.8 ± 3.7 mmol/L; n = 309) indicating a low proportion of carbonate dissolution. Additionally, the comparison of $^{14}C_{DIC}$ and $\delta^{13}C$ values of DIC with potential calculated equilibrium inputs (Fig. 2) shows that there is no trend towards carbonate dissolution along the groundwater flow path. In this system, it is likely that most of the carbonate mineral reactions occur in the unsaturated zone under open system conditions with respect to soil $CO_{2(g)}$. Therefore the $\delta^{13}C$ value in groundwater in the Southern Perth Basin ($\delta^{13}C \approx -21.4 \pm 2‰$; Fig. 2) appears to be due to dissolution of soil $CO_{2(g)}$ and some dissociation into bicarbonate in recharging groundwater. Whereas in the Northern Perth Basin and Central Perth Basin there appears to be additional fractionation of $\delta^{13}C$ ($\delta^{13}C \approx -17.6 \pm 2‰$ and $\delta^{13}C \approx -15.0 \pm 3‰$, respectively; Fig. 2) suggesting it has moved from open to closed system conditions. This could be the result of fractionation during CO_2 hydration and speciation (Clark and Fritz, 1997), or alternatively it could be the result of anthropogenic groundwater mixing not identified by the quality control procedure, which will be discussed further in section 4.2.2.

The groundwater $\delta^{13}C$ values of DIC do not seem to be temporally or spatially controlled as there is no systematic change in $\delta^{13}C$ with $^{14}C_{DIC}$ (approximation of groundwater residence time in Fig. 2), except for wells in the Southern Perth Basin where groundwater samples with $^{14}C_{DIC}$ <10 pMC have slightly higher $\delta^{13}C$ values ($\delta^{13}C \approx -20.1 \pm 1‰$; Fig. 2) which could represent a change in $^{13}C/^{12}C$ input, or additional fractionation of $\delta^{13}C$. The $^{14}C_{DIC}$ values decrease from 100 pMC to background with no change in $\delta^{13}C$ values variability (Fig. 2), thus suggesting the $^{14}C_{DIC}$ decrease is attributed to radiocarbon decay throughout the Perth Basin. This provides further confidence for using the Perth Basin $^{14}C_{DIC}$ values for groundwater residence time estimations.

The uncorrected and corrected $^{14}C_{DIC}$ ages for the groundwater samples calibrated to years before present are presented in Supplementary Electronic data file 2. The geochemical adjustment models were calculated assuming that the initial $^{14}C_{DIC}$ input is 100 pMC, the soil CO_2 gas $\delta^{13}C$ value is $-24‰$, and carbonate $\delta^{13}C$ value is $-2‰$ to represent terrestrial deposited calcite (Clark and Fritz, 1997; Salomons and Mook, 1986). The $^{14}C_{DIC}$ mean residence times calculated using the Pearson's and Han and Plummer's geochemical adjustment models had an average difference of 380 years (range of 4 to 1889 years which generally increases with $^{14}C_{DIC}$ age; Supplementary Electronic data file 2) and as the Han and Plummer's geochemical adjustment model is a combination of three models it was considered the most representative for this work.

4.2. Groundwater $\delta^{18}O$ and δ^2H values in the Perth Basin

Groundwater $\delta^{18}O$ and δ^2H values from the Northern Perth Basin, Central Perth Basin and Southern Perth Basin are plotted with the modern Perth Meteoric Water Line (PMWL) in Fig. 3a-c. The groundwater data plot along the PMWL in all three sections of the Perth Basin (Fig. 3). Plotted also are $\delta^{18}O$ and δ^2H values of weighted mean summer (December–February) and winter

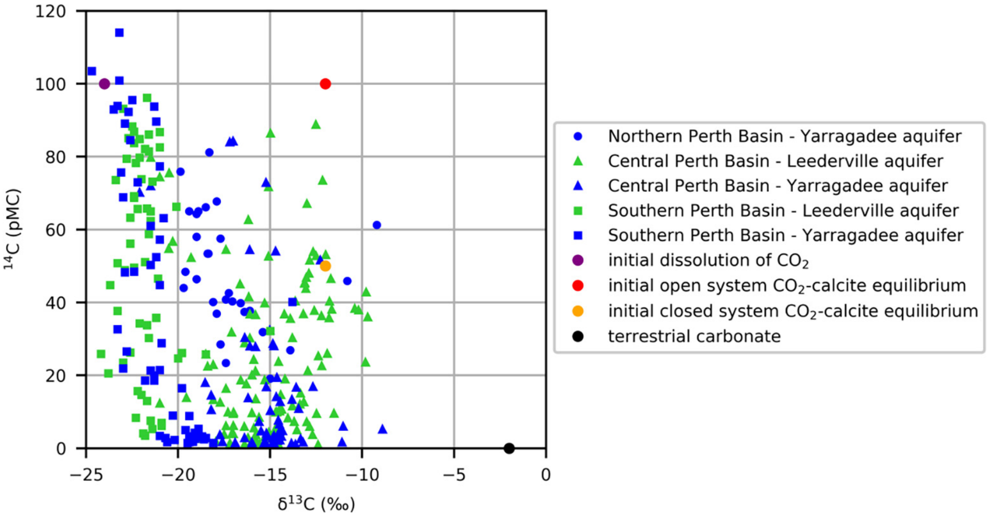

Fig. 2. $^{14}C_{DIC}$ against $\delta^{13}C$ for Northern Perth Basin, Central Perth Basin and Southern Perth Basin with calculated equilibrium inputs assuming that the initial soil CO_2 gas ^{14}C input is 100 pMC and $\delta^{13}C$ input is $-24‰$, and terrestrial calcite $\delta^{13}C$ is $-2‰$ (Clark and Fritz, 1997; Salomons and Mook, 1986).

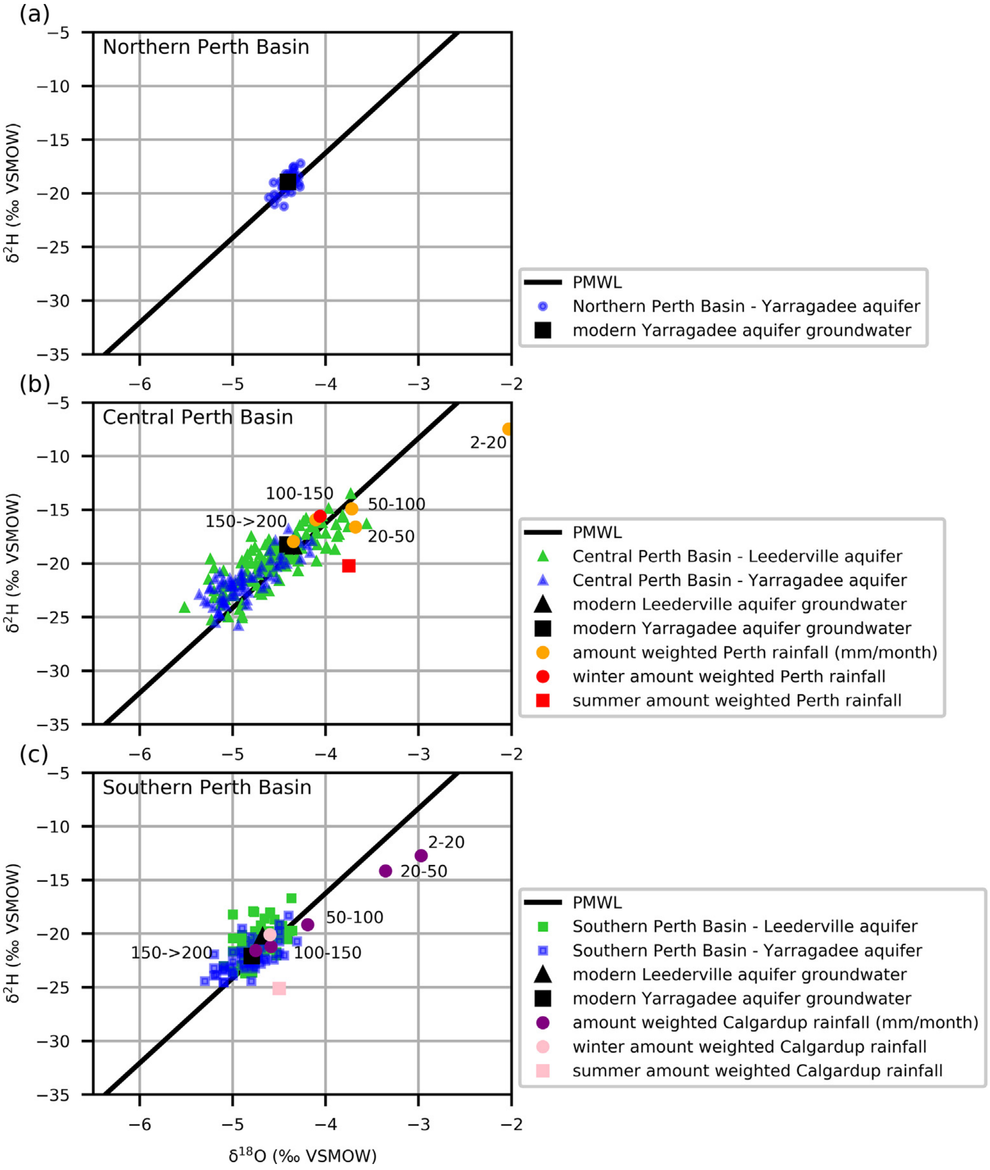

Fig. 3. Groundwater δ^2H against δ^{18}O from the Leederville aquifer and Yarragadee aquifer with Perth Meteoric Water Line (PMWL; $\delta^2H = 7.91\delta^{18}O + 15.42$) for (a) Northern Perth Basin, (b) Central Perth Basin and (c) Southern Perth Basin. The amount weighted mean summer (December–February) and winter (June–August) rainfall, as well as monthly amount weighted rainfall averages labelled with the rainfall range in mm/month where >100 mm/month are comprised of >10 days of rainfall at Perth (Hollins et al., 2018) and Calgardup Caves (Griffiths et al., Unpublished results) are included for the Central Perth Basin (b) and Southern Perth Basin (c), respectively.

(June–August) rainfall, as well as monthly amount weighted rainfall averages for Perth (Fig. 3b) and Calgardup Caves (Fig. 3c). The groundwater data align with the winter weighted rainfall δ^{18}O values, versus the summer weighted rainfall δ^{18}O value, as expected since winter months typically have >100 mm of rainfall (Fig. 3b and 3c). Indeed much of the groundwater isotopic data plot lower than the >100 mm/month isotopic values (Fig. 3b and 3c).

4.2.1. Modern groundwater and rainfall

Modern monthly and annual rainfall isotope data for Perth and Calgardup Caves are presented in Fig. 4. In Perth the weighted mean annual rainfall δ^{18}O is −4.0 ± 0.1‰ and d-excess is 15.8 ± 0.5‰ (Fig. 4; Hollins et al., 2018), and at Calgardup Caves weighted mean annual rainfall δ^{18}O is −4.5 ± 0.5‰ and d-excess is 15.4 ± 1.3‰ (Fig. 4; Griffiths et al., Unpublished results).

Modern groundwater ($^{14}C_{DIC}$ age = 0 ka) δ^{18}O values in the Central Perth Basin and Northern Perth Basin are −4.3 ± 0.3‰ and −4.4 ± 0.1‰, respectively, and in the Southern Perth Basin are −4.7 ± 0.1‰ (Fig. 3a-c). Thus the modern groundwater δ^{18}O values reflect a N-S gradient that is consistent with Perth and Calgardup Caves weighted mean annual rainfall (Fig. 3).

It is clear from the amount weighted rainfall values in Fig. 3b and 3c that modern groundwater in the Perth Basin (e.g. δ^{18}O = -4.7 ± 0.1‰ and d-excess = 16.9 ± 1.6‰ in Southern Perth Basin; Fig. 3c) is recharged during the winter months with high intensity rainfall rates >100 mm/month (δ^{18}O <-4.4‰ and d-excess >15‰; Fig. 3c). Wetter months tend to be dominated by higher intensity rainfall events which tend to be depleted in ^{18}O in south-west Australia (Fig. 4a), as well as the majority of Australia, due to the amount effect (Dansgaard, 1964; Hollins et al., 2018). This amount effect is particularly dominant in south-west Australia (Treble et al., 2005a) and other potential mechanisms such as source and trajectory effects have a relatively small impact on isotopic composition (Griffiths et al., Unpublished results). This implies that groundwater recharge in the Perth Basin is more likely occurring as a result of high intensity rainfall which may produce a large

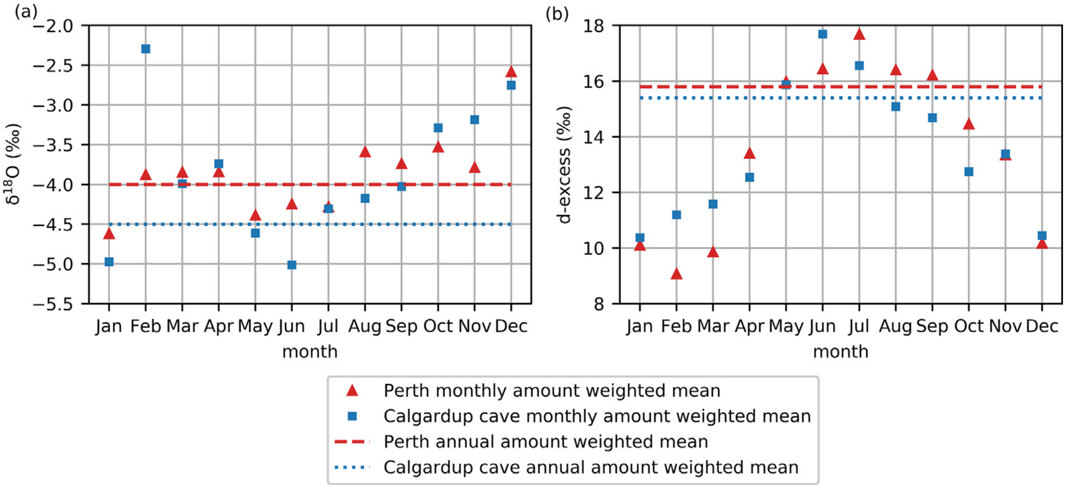

Fig. 4. Monthly and annual average rainfall isotope data for Perth (Hollins et al., 2018) and Calgardup Cave (Griffiths et al., Unpublished results) for (a) δ^{18}O and (b) d-excess.

volume of water in a relatively short amount of time and these are more effective in terms of producing runoff and hence recharge. Thus the modern groundwater isotopic data is biased to high volume and intense rainfall months with a seasonal bias to winter being archived as groundwater, similarly found in other groundwater studies (Bryan et al., 2016; Hollins et al., 2018; Jasechko et al., 2014).

Both the modern and palaeo-groundwater δ^{18}O and δ^{2}H data plot along the PMWL (Fig. 3a-c) indicating that the modern rainfall-recharge isotopic relationships are relatively consistent through time. This implies that the Leederville aquifer and Yarragadee aquifer palaeo-groundwater samples were similarly recharged by high magnitude winter rainfall.

4.2.2. Groundwater δ^{18}O values through time

Groundwater isotopic variability through time is shown for the interpreted flow line derived data in Fig. 5a-c, and the regional datasets in Fig. 5d-f, for the Leederville aquifer and Yarragadee aquifer in each of the Northern Perth Basin, Central Perth Basin and Southern Perth Basin regions. The LOESS curves from the regional datasets are reproduced with the flow line data for comparison (Fig. 5a-c). Considering the numerical smoothing applied in this study to visualise average groundwater δ^{18}O trends, and the averaging effect of dispersion, it is possible that the lowest/highest groundwater δ^{18}O may be more indicative of the actual recharge extremes for a particular period. For example, the sample δ^{18}O minimum of −5.1‰ at 4 ka (Fig. 5f) may be more representative of recharge values at that time. Nevertheless, there is general agreement between the regional LOESS curves and interpreted flow line data in terms of mean δ^{18}O values and trends (Fig. 5a-c). The general agreement between the regional and interpreted flow line δ^{18}O trends supports the robustness of the regional datasets to reconstruct the isotopic variability of rainfall recharge through time. Overall, the agreement is better for the Northern Perth Basin and Southern Perth Basin, and poorer for the Central Perth Basin which is dominated by greater isotopic variability, which is discussed further below.

In the Northern Perth Basin groundwater δ^{18}O values of approximately −4.4‰ in the Yarragadee aquifer appear to have been relatively constant during the last 10 ka (Fig. 5d). The groundwater samples older than 10 ka were excluded because they showed evidence of mixing with older saline water (9 of 38 samples were excluded; Supplementary Material). As the aquifer in this region is unconfined it is possible that the groundwater isotopic values in Fig. 5d may represent an averaged signal of δ^{18}O for the Holocene.

In the Central Perth Basin groundwater δ^{18}O values in the Leederville aquifer range from −3.6‰ to −5.5‰ over 35 ka (Fig. 5e). In the Yarragadee aquifer groundwater δ^{18}O values range from −4.2‰ to −5.4‰; however there is a more definitive trend of δ^{18}O rising with time (Fig. 5e). Thus there is a ~0.5‰ offset between the Leederville aquifer and Yarragadee aquifer LOESS curves prior to 5 ka (Fig. 5e). The considerable scatter in the Leederville aquifer δ^{18}O data (standard deviation >0.3‰), compared to the Yarragadee aquifer δ^{18}O data (standard deviation ≤0.3‰) for the Central Perth Basin, implies that the Leederville aquifer may be an unreliable dataset for examining multi-millennial trends in recharge δ^{18}O. Some of the scatter in the Central Perth Basin δ^{18}O values are probably a result of groundwater abstraction modifying natural groundwater flow directions in the well fields (Supplementary Material A2; Davidson and Yu, 2006; CSIRO, 2009). Groundwater abstraction may cause mixing, and hence scatter in the δ^{18}O record, which will also give mixed and potentially misleading ^{14}C$_{DIC}$ ages (Fig. 5b and 5e; Han and Plummer, 2016). Therefore, the Central Perth Basin Leederville aquifer groundwater isotopic record is unlikely to represent recharge and thus is not used as a palaeo-recharge archive. However, the deeper more confined Central Perth Basin Yarragadee aquifer groundwater isotopic record is likely to be a more reliable archive.

In the Southern Perth Basin groundwater δ^{18}O values in the Leederville aquifer range from −4.4‰ to −5.1‰ and in the Yarragadee aquifer groundwater δ^{18}O values similarly range from −4.3‰ to −5.3‰ (Fig. 5f). Both aquifers show a clear common trend in the groundwater δ^{18}O values. In the Yarragadee aquifer, groundwater δ^{18}O values are approximately −5.2‰ at 35 ka and increase to −4.5‰ by approximately 15 ka, before decreasing to modern values (-4.7‰; Fig. 5f). The δ^{18}O mean and trends in the Leederville aquifer are similar but show more detailed changes through the Holocene. The Leederville aquifer follows the Yarragadee aquifer values rising to −4.5‰ at 15 ka but the Leederville aquifer remain at this value until 10 ka before declining to −4.8‰ by 4 ka and then recovering to modern values similar to the Yarragadee aquifer. Thus the Leederville aquifer data suggest a broad Early Holocene isotopic maxima and a Mid- to Late Holocene isotopic minima when δ^{18}O values were higher and lower, respectively, relative to modern groundwater values. Considering the relatively tight spread of groundwater δ^{18}O values comprising the LOESS trend and that the δ^{18}O trends are supported in the groundwater flow line data, it is hypothesised that the groundwater δ^{18}O LOESS curves in the Southern Perth Basin, especially in the Leederville aquifer, are an isotopic archive of past variability in

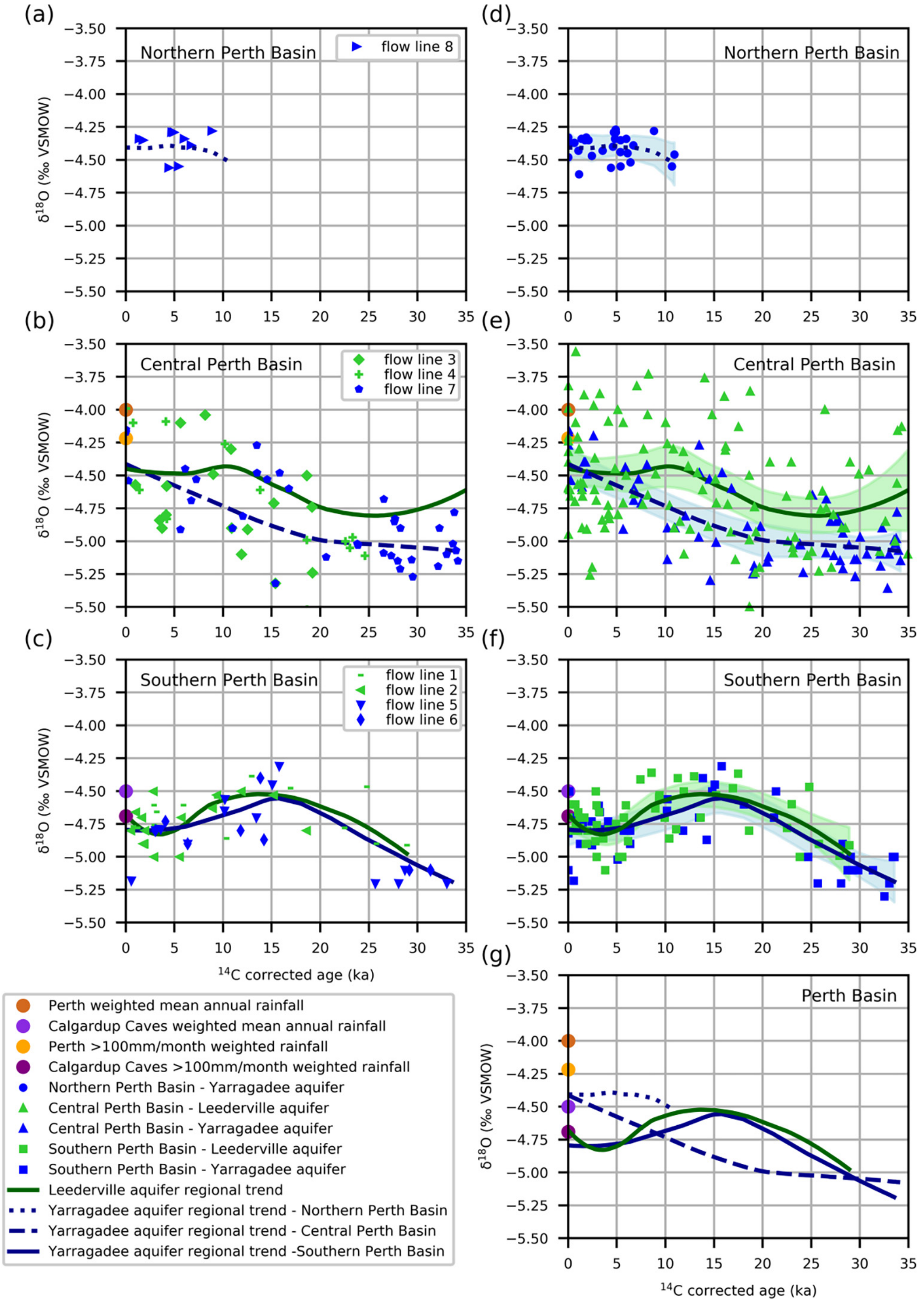

Fig. 5. $\delta^{18}O$ values along flow lines in the Leederville aquifer and Yarragadee aquifer for the (a) Northern Perth Basin, (b) Central Perth Basin, and (c) Southern Perth Basin. The regional $\delta^{18}O$ datasets, which includes the flow line data, are plotted for the (d) Northern Perth Basin, (e) Central Perth Basin, and (f) Southern Perth Basin. Regional trend lines are the smoothed LOESS curves of the regional Leederville aquifer and Yarragadee aquifer datasets. The green and blue shaded area surrounding the regional trend lines represent 95% confidence intervals. For all plots green represents the Leederville aquifer and blue represents the Yarragadee aquifer. (g) Superimposed regional trend lines for Northern Perth Basin, Central Perth Basin and Southern Perth Basin.

groundwater recharge. Also, it is important to note that as groundwater systems are slow to respond, it is the point of inflexion of the isotopic trends that likely indicate a change of state.

4.2.3. Pleistocene groundwater and climate

Groundwater $\delta^{18}O$ values are lowest in the record in the Yarragadee aquifer between 35 and 30 ka for both the Central and Southern Perth Basin, by approximately 0.5‰ relative to modern (Fig. 5g). Lower groundwater $\delta^{18}O$ values during this time have also been observed in the Sydney Basin (~1‰ lower; Cendón et al., 2014; Jasechko et al., 2015) in agreement with those recorded for the Perth Basin. The Southern Perth Basin groundwater $\delta^{18}O$ values rise smoothly by over 0.75‰ until 15 ka, whereas in the Central Perth Basin groundwater $\delta^{18}O$ values remain low until 20 ka. There appears to be no clear defining feature(s) during peak LGM conditions (~22–18 ka) in either dataset. Trends in the

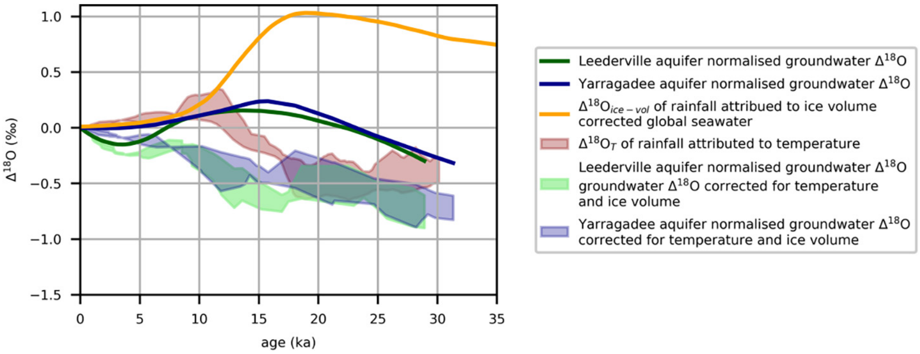

Fig. 6. Normalised groundwater $\Delta^{18}O$ relative to modern values for Yarragadee aquifer and Leederville aquifer in Southern Perth Basin. Potential rainfall $\Delta^{18}O_T$ as a response to temperature changes calculated from the sea-surface temperature record of Calvo et al., (2007) and Pahnke and Sachs, (2006) using the method in Horita and Wesolowski, (1994), and seawater ^{18}O variations, $\Delta^{18}O_{Ice\text{-}vol}$, calculated by Bintanja and Wal, (2008) are also plotted. The estimated residual $\Delta^{18}O$ variation in groundwater accounting for temperature and seawater $\delta^{18}O$ effects are also plotted for Southern Perth Basin Yarragadee aquifer and Leederville aquifer.

Leederville aquifer are in agreement with the Yarragadee aquifer for the Southern Perth Basin.

Interpretation of groundwater isotopic values during the Late Pleistocene is not straight-forward since in addition to variations in local climate, the isotopic values will also be impacted by: 1) the change in seawater isotopic values due to enhanced storage of the lighter isotopes in glacial ice (Bintanja and Wal, 2008); 2) reduced global temperatures (Calvo et al., 2007; Pahnke and Sachs, 2006); and 3) potentially, changes to the trajectories of air masses owing to the exposure of continental shelves. This latter point is considered to be minor for this location as the LGM coastline is estimated to be between 20 and 85 km from the current coastline; and the associated isotopic impact of increased continental rainout effect would be only up to 0.1‰ for this distance (Hollins et al., 2018). However, this may have possibly affected the groundwater flow and discharge rates due to the exposure of continental shelves. There is no evidence of mixing due to this in the dataset but these effects would need to be examined in more detail using hydrology and geochemical modelling.

The isotopic impact of increased glacial ice ($\Delta^{18}O_{ice\text{-}vol}$; Bintanja and Wal, 2008) and reduced temperature ($\Delta^{18}O_T$; Calvo et al., 2007; Pahnke and Sachs, 2006; Horita and Wesolowski, 1994) are quantified (see section 3.4; Supplementary Material Fig. S3) and compared for the Southern Perth Basin groundwater $\delta^{18}O$ on a normalised scale, $\Delta^{18}O$, where $\Delta^{18}O$ represents the deviation from the modern value (Fig. 6). These corrections are necessary in order to interpret potential changes in groundwater $\delta^{18}O$ through time as a palaeoclimate archive, i.e. in order to estimate the direction and magnitude of isotopic change that may be attributed to changes in local and regional hydroclimate. However, these two effects present opposing and similar magnitude isotopic corrections (Fig. 6) such that the resulting correction is not large (approximately 0.5‰ lower at 30 ka and through the deglaciation). This emphasises that recharge to groundwater has been via high volume/high intensity rainfall events throughout the last 35 ka.

Thus the data suggest that groundwater has been recharged by high volume/high intensity rainfall throughout the Late Pleistocene and Holocene, as it is for the modern system. Today, modern rainfall isotopic studies show that high volume/high intensity rainfall events with low $\delta^{18}O$ values in southern Australia typically occur as a result of low pressure systems embedded in the westerly wind flow tracking close to the site (Barras and Simmonds, 2009; Treble et al., 2005b). This supports that groundwater recharge to the Southern and Central Perth Basins has been maintained via the westerly systems throughout the last 35 ka. According to the amount effect in this region, the somewhat lower isotopic values from 35 to 15 ka in the corrected $\Delta^{18}O$ values could be argued to indicate an increase in the volume/intensity of events in this period. This could be consistent with a northward displacement of the Walker and Hadley Circulations during the LGM (Mohtadi et al., 2011). However, the predominance of the amount effect over the source and trajectory effects in this region (Griffiths et al., Unpublished results), prevents using the isotopes to identify moisture source region. Thus more northerly sourced rainfall, similarly cannot be excluded; although we note that there is evidence of decreased cyclone and monsoon conditions during the LGM (De Deckker et al., 2014; May et al., 2015; Reeves et al., 2013). Additionally, the effects of recharge thresholds are considered below.

Changes in recharge thresholds could also potentially cause a shift in the isotopic value of groundwater recharge since soil moisture, as well as vegetation type and distribution could alter the distribution of rainfall events that lead to runoff and recharge (Phillips et al., 2013). It may be that the small rise in groundwater $\delta^{18}O$ during the deglaciation is related to changing rainfall and river recharge thresholds, and that the difference in the timing of this response between the Central and Southern Perth Basins is related to these recharge thresholds. This would imply that recharge threshold conditions favoured recharge by higher volume/higher intensity rainfall relative to conditions for the Holocene and today. This is consistent with vegetation proxy studies within south-west Australia showing evidence of a ‘drier’ soil moisture zone during the LGM (Burke, 2004; Dortch, 2004; Faith et al., 2017; Lipar and Webb, 2014; Petherick et al., 2013; Shulmeister et al., 2004; Sniderman et al., 2019; Wyrwoll et al., 2000), i.e. a drier soil moisture zone facilitates recharge from only those higher volume/higher intensity rainfall events.

During the deglaciation there is a subsequent rise in $\delta^{18}O$, which likely indicates a relative reduction in the intensity or volume of rainfall leading to recharge. However, the datasets diverge in their timing between the Central and Southern Perth Basins (comparing the Yarragadee aquifers; Fig. 5g). Nevertheless, the data suggest a shift to lower volume and/or intensity rainfall leading to recharge by approximately 10 ka in the Southern Perth Basin and Central Perth Basin. A change in recharge thresholds from temperature alone is unlikely because the change in groundwater $\delta^{18}O$ is slow relative to the rapid global temperature rise. Instead this change could be due to either a change in rainfall characteristics, or changes in recharge thresholds which may also be related to climate e.g. soil moisture content, evapotranspiration, etc.

4.2.4. Holocene groundwater and climate

Throughout the Holocene the Northern Perth Basin have groundwater $\delta^{18}O$ values of −4.4 ± 0.1‰ that are approximately 0.4‰ higher than the Southern Perth Basin (Fig. 5g) again consistent with the N-S gradient in modern groundwater and rainfall values. The Leederville aquifer data for the Central Perth Basin is considered unreliable and the response in the Yarragadee aquifer has been discussed above. A final observation for these data is the trend towards lower δ^{18}O in the Southern Perth Basin in the Mid- to Late Holocene (Fig. 5f). At this time, Southern Perth Basin groundwater is approximately −4.8‰ as indicated by the LOESS curve, and as low as −5.1‰ if individual data points are considered. The trend of lower δ^{18}O groundwater values in the Mid- to Late Holocene cannot be explained by temperature and ice volume changes alone as these are estimated to have contributed little to no change to Holocene groundwater isotopic values (Fig. 6). Also, such effects would contribute to all of the Perth Basin records not just the Southern Perth Basin. Instead, the 'amount effect' prevalence in this region (Fischer and Treble, 2008; Griffiths et al., Unpublished results; Hollins et al., 2018; Treble et al., 2005b) implies that recharge was occurring by high volume and/or more intense rainfall, relative to today during the Mid- to Late Holocene. This is supported by evidence for an increase in effective rainfall supported by increased canopy height from 10 ka within the Southern Perth Basin (Dortch, 2004), and an increase in effective precipitation from 4.8 ka interpreted from pollen and fossil charcoal from two nearby peat profiles (Dodson and Lu, 2000).

5. Conclusions

The groundwater isotopic record is an archive of recharge, and hence an indicator of rainfall and climatic conditions generating groundwater recharge. It represents an isotopic palaeo-recharge record which is long and continuous, but low resolution. Given that the current records for south-west Australia cover smaller periods of time, this is the first long, continuous palaeo-recharge record for this region.

The modern groundwater and rainfall isotopic values indicate that groundwater in south-west Australia is recharged by high volume/high intensity winter rainfall from the westerly winds. The long-term dataset presented here suggests that this has been the case for the last 35 ka. Somewhat lower isotopic values between 35 and ~10 ka indicate that it is possible that recharge was by relatively higher volume/higher intensity rainfall. This may well be a direct function of changes in the distribution of rainfall intensity during this time period relative to today, i.e, more intense rainfall, but vegetation structure and soil moisture may also have contributed to changes in rainfall and river recharge thresholds that determine groundwater recharge. The Southern Perth Basin groundwater isotopic record also indicates a trend towards higher volume and/or intense rainfall during the Mid- to Late Holocene.

There are no obvious long duration hiatuses in recharge supporting relatively continuous recharge over the last ~35 ka; however, the actual volume of recharge may have changed due to changes in climate and rainfall. From the water isotopes alone it is not possible to interpret the volume of groundwater recharged by these changes, thus a future study using other methods, such as modelling is required. Future research is also required to model the influence of rainfall and recharge thresholds for past climate states to better understand their interactions and the groundwater δ^{18}O data presented here could be a target dataset for this.

Linking the groundwater isotopic record with groundwater recharge and changes in rainfall intensity, and in the future recharge volume, is important for an improved understanding of palaeo-recharge which can be used to improve 'sustainable' use of current groundwater resources. Additionally, the links between rainfall intensity changes, hence changes in climate, and groundwater recharge is an important contribution to improving palaeoclimate-groundwater models which can be used to improve model predictions of future climate and groundwater recharge changes in south-west Australia. Furthermore, this can be undertaken on other groundwater basins with sufficient groundwater δ^{18}O, δ^{2}H and radioisotope measurements and appropriate flow conditions. Additionally, this could be combined with trace elements in speleothems (for example, Nagra et al., 2017) to provide shallow vadose zone recharge estimates, as well as other records to determine climate variables.

CRediT authorship contribution statement

Stacey C. Priestley: Conceptualization, Methodology, Writing - original draft. **Karina T. Meredith:** Conceptualization, Methodology, Writing - review & editing. **Pauline C. Treble:** Conceptualization, Methodology, Writing - review & editing. **Dioni I. Cendón:** Conceptualization, Writing - review & editing. **Alan D. Griffiths:** Conceptualization, Resources, Writing - review & editing. **Suzanne E. Hollins:** Conceptualization, Writing - review & editing. **Andy Baker:** Conceptualization, Writing - review & editing. **Jon-Philippe Pigois:** Resources.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.135105.

References

AECOM, 2015. Hydrochemical and isotopic assessment Leederville & Yarragadee aquifers of the Perth Basin, WA. Department of Water, Perth Western Australia.

Ali, R., McFarlane, D., Varma, S., Dawes, W., Emelyanova, I., Hodgson, G., et al., 2012. Potential climate change impacts on groundwater resources of south-western Australia. J. Hydrol. 475, 456–472. https://doi.org/10.1016/j.jhydrol.2012.04.043.

Baddock, L., Vine, J., Leathersich, M., 2005. South West Yarragadee hydrogeological investigations and evaluation Southern Perth Basin. Infrastructure Planning Branch, Western Australia.

Bard, E., Arnold, M., Hamelin, B., Tisnerat-Laborde, N., Cabioch, G., 1998. Radiocarbon calibration by means of mass spectrometric ^{230}Th/^{234}U and ^{14}C Ages of corals: An updated database including samples from Barbados, Mururoa and Tahiti. Radiocarbon 40, 1085–1092. https://doi.org/10.1017/S0033822200019135.

Barras, V., Simmonds, I., 2009. Observation and modeling of stable water isotopes as diagnostics of rainfall dynamics over southeastern Australia. J. Geophys. Res. Atmos. 114. https://doi.org/10.1029/2009JD012132.

Barron, O., Silberstein, R., Ali, R., Donohue, R., McFarlane, D.J., Davies, P., et al., 2012. Climate change effects on water-dependent ecosystems in south-western Australia. J. Hydrol. 434–435, 95–109. https://doi.org/10.1016/j.jhydrol.2012.02.028.

Bates, B.C., Hope, P., Ryan, B., Smith, I., Charles, S., 2008. Key findings from the Indian Ocean Climate Initiative and their impact on policy development in Australia. Climatic Change 89, 339–354. https://doi.org/10.1007/s10584-007-9390-9.

Bintanja, R., Wal, R.S.W., 2008. North American ice-sheet dynamics and the onset of 100,000-year glacial cycles. Nature 454, 869–872. https://doi.org/10.1038/nature07158.

Bryan, E., Meredith, K.T., Baker, A., Post, V.E.A., Andersen, M.S., 2016. Island groundwater resources, impacts of abstraction and a drying climate: Rottnest Island, Western Australia. J. Hydrol. 542, 704–718. https://doi.org/10.1016/j.jhydrol.2016.09.043.

Bureau of Meterology, 2019. Climate Data Online. Geraldton Airport Monthly Climate Statistics. Accessed August 2019 http://www.bom.gov.au/climate/averages/tables/cw_008051.shtml.

Burke, S., 2004. The feasibility of using charcoal from Devil's Lair, South-West Australia, to access human responses to vegetation changes at the Late Pleistocene-Holocene boundary. Aust. Archaeol. 59, 62–64. https://doi.org/10.1080/03122417.2004.11681793.

Calvo, E., Pelejero, C., De Deckker, P., Logan, G.A., 2007. Antarctic deglacial pattern in a 30 kyr record of sea surface temperature offshore South Australia. Geophys. Res. Lett. 34. https://doi.org/10.1029/2007GL029937.

Cartwright, I., Weaver, T.R., Cendón, D.I., Fifield, L.K., Tweed, S.O., Petrides, B., et al., 2012. Constraining groundwater flow, residence times, inter-aquifer mixing, and aquifer properties using environmental isotopes in the southeast Murray Basin, Australia. Appl. Geochem. 27, 1698–1709. https://doi.org/10.1016/j.apgeochem.2012.02.006.

Cendón, D.I., Hankin, S.I., Williams, J.P., Van der Ley, M., Peterson, M., Hughes, C.E., et al., 2014. Groundwater residence time in a dissected and weathered sandstone plateau: Kulnura-Mangrove Mountain aquifer, NSW, Australia. Aust. J. Earth Sci. 61, 475–499. https://doi.org/10.1080/08120099.2014.893628.

Clark, I., Fritz, P., 1997. Environmental isotopes in hydrogeology. CRC Press, New York.

Cleveland, W.S., Grosse, E., Shyu, M.J., 1992. Local regression models. In: Chambers, J.M., Hastie, T. (Eds.), Statistical models in S. Chapman and Hall, New York, pp. 309–376.

CSIRO, 2009. Groundwater yields in south-west Western Australia. A report to the Australian Government from the CSIRO South-West Western Australia Sustainable Yields Project. CSIRO Water for a Healthy Country Flagship, Australia.

Dansgaard, W., 1964. Stable isotopes in precipiation. Tellus 16, 436–1408.

Davidson, W.A., Yu, X., 2006. Perth regional aquifer modelling system (PRAMS) model development: Hydrogeology and groundwater modelling. Department of Water, Western Australia.

De Deckker, P., Barrows, T.T., Rogers, J., 2014. Land-sea correlations in the Australian region: Post-glacial onset of the monsoon in northwestern Western Australia. Quat. Sci. Rev. 105, 181–194. https://doi.org/10.1016/j.quascirev.2014.09.030.

Department of Mines and Petroleum, 2014. Summary of petroleum prospectivity: Perth Basin. Government of Western Australia, Perth, Western Australia.

Department of Water, 2017a. Groundwater chemistry and isotope survey, Perth, Western Australia. Government of Western Australia, Perth, Western Australia.

Department of Water, 2017b. Northern Perth Basin: Geology, hydrogeology and groundwater resources. Hydrogeological bulletin series, report no. HB1. Government of Western Australia, Perth, Western Australia.

Dodson, J.R., Lu, J.J., 2000. A Late Holocene vegetation and environment record from Byenup Lagoon, south-western Australia. Aust. Geogr. 31, 41–54. https://doi.org/10.1080/00049180093529.

Dortch, J., 2004. Late Quaternary vegetation change and the extinction of Black-flanked Rock-wallaby (Petrogale lateralis) at Tunnel Cave, southwestern Australia. Palaeogeogr. Palaeoclimatol. Palaeoecol. 211, 185–204. https://doi.org/10.1016/j.palaeo.2004.05.005.

Edmunds, W.M., 2005. Groundwater as an archive of climatic and environmental change. In: Aggarwal, P.K., Gat, J.R., Froehlich, K. (Eds.), Isotopes in the water cycle past, present and future of a developing science. Springer Netherlands, pp. 341–352.

E.G.I.S. Consulting, 1999. Isotope hydrogeology of the confined aquifers in the Northern Perth Basin, Western Australia. Water and Rivers Commission, Western Australia.

Fairbanks, R.G., Mortlock, R.A., Chiu, T.-C., Cao, L., Kaplan, A., Guilderson, T.P., et al., 2005. Radiocarbon calibration curve spanning 0 to 50,000 years BP based on paired ^{230}Th/^{234}U/^{238}U and ^{14}C dates on pristine corals. Quat. Sci. Rev. 24, 1781–1796. https://doi.org/10.1016/j.quascirev.2005.04.007.

Faith, J.T., Dortch, J., Jones, C., Shulmeister, J., Travouillon, K.J., 2017. Large mammal species richness and Late Quaternary precipitation change in south-western Australia. J. Quaternary Sci. 32, 760–769. https://doi.org/10.1002/jqs.2888.

Fischer, M.J., Treble, P.C., 2008. Calibrating climate-δ^{18}O regression models for the interpretation of high-resolution speleothem δ^{18}O time series. J. Geophys. Res. Atmos. 113. https://doi.org/10.1029/2007JD009694.

Gouramanis, C., Dodson, J., Wilkins, D., De Deckker, P., Chase, B.M., 2012. Holocene palaeoclimate and sea level fluctuation recorded from the coastal Barker Swamp, Rottnest Island, south-western Western Australia. Quat. Sci. Rev. 54, 40–57. https://doi.org/10.1016/j.quascirev.2012.05.007.

Griffiths, A., Treble, P., et al., Unpublished results. A decade of precipitation stable water isotope variability in coastal southwestern Western Australia. (in preperation)

Haldorsen, S., Van Der Ploeg, M.J., Cendón, D.I., Chen, J., Jemâa, N.C.B., Gurdak, J.J., et al., 2016. Groundwater and global palaeoclimate signals (G@GPS). Episodes 39, 556–567 https://doi.org/10.18814/epiiugs/2016/v39i4/103888.

Han, L.F., Plummer, L.N., 2013. Revision of Fontes & Garnier's model for the initial C-14 content of dissolved inorganic carbon used in groundwater dating. Chem. Geol. 351, 105–114. https://doi.org/10.1016/j.chemgeo.2013.05.011.

Han, L.F., Plummer, L.N., 2016. A review of single-sample-based models and other approaches for radiocarbon dating of dissolved inorganic carbon in groundwater. Earth-Sci. Rev. 152, 119–142. https://doi.org/10.1016/j.earscirev.2015.11.004.

Harrington, G.A., Gardner, W.P., Smerdon, B.D., Hendry, M.J., 2013. Palaeohydrological insights from natural tracer profiles in aquitard porewater, Great Artesian Basin. Australia. Water Resour. Res. 49, 4054–4069. https://doi.org/10.1002/wrcr.20327.

Harrington, G.A., Macaulay, S., Johnston, C., 2015. Groundwater chemistry and isotope survey for the Murray-Peel Groundwater Project Area. Department of Water, Perth, Western Australia.

Hendry, M.J., Barbour, S.L., Novakowski, K., Wassenaar, L.I., 2013. Paleohydrogeology of the Cretaceous sediments of the Williston Basin using stable isotopes of water. Water Resour. Res. 49. https://doi.org/10.1002/wrcr.20321.

Hollins, S.E., Hughes, C.E., Crawford, J., Cendón, D.I., Meredith, K.T., 2018. Rainfall isotope variations over the Australian continent – Implications for hydrology and isoscape applications. Sci. Total Environ. 645, 630–645. https://doi.org/10.1016/j.scitotenv.2018.07.082.

Hope, P.K., Drosdowsky, W., Nicholls, N., 2006. Shifts in the synoptic systems influencing southwest Western Australia. Clim. Dynam. 26, 751–764. https://doi.org/10.1007/s00382-006-0115-y.

Horita, J., Wesolowski, D.J., 1994. Liquid-vapor fractionation of oxygen and hydrogen isotopes of water from the freezing to the critical temperature. Geochim. Cosmochim. Acta 58, 3425–3437. https://doi.org/10.1016/0016-7037(94)90096-5.

Ingerson Jr., E., 1964. Estimation of age and rate of motion of groundwater by the ^{14}C method. In: Sugawara, K., Koyama, T., Miyake, Y. (Eds.), Recent Researches in the fields of hydrosphere, atmosphere and nuclear geochemistry. Editorial Committee for Sugawara, pp. 263–283.

Jasechko, S., Birks, S.J., Gleeson, T., Wada, Y., Fawcett, P.J., Sharp, Z.D., et al., 2014. The pronounced seasonality of global groundwater recharge. Water Resour. Res. 50, 8845–8867. https://doi.org/10.1002/2014WR015809.

Jasechko, S., Lechler, A., Pausata, F.S.R., Fawcett, P.J., Gleeson, T., Cendón, D.I., et al., 2015. Late-glacial to Late-Holocene shifts in global precipitation δ^{18}O. Clim. Past 11, 1375–1393. https://doi.org/10.5194/cp-11-1375-2015.

Jiráková, H., Huneau, F., Celle-Jeanton, H., Hrkal, Z., Le Coustumer, P., 2011. Insights into palaeorecharge conditions for European deep aquifers. Hydrogeol. J. 19, 1545–1562. https://doi.org/10.1007/s10040-011-0765-7.

Kalin, R.M., 2000. Radiocarbon dating of groundwater systems. In: Cook, P.G., Herczeg, A.L. (Eds.), Environmental tracers in subsurface hydrology. Springer Science+Business Media, New York.

Kern, A., Koomberi, H., 2010. Hydrogeology of the Coastal Plain between Geraldton and Dongara. Department of Water, Perth, Western Australia.

Kitagawa, H., van der Plicht, J., 1998. Atmospheric radiocarbon calibration to 45,000 yr B.P.: Late Glacial fluctuations and cosmogenic isotope production. Science 279, 1187–1190. https://doi.org/10.1126/science.279.5354.1187.

Leaney, F., 2004. Groundwater ^{14}C ages for the Confined Aquifers in the Southern Perth Basin, Western Australia. Water Corporation, W.A., Western Australia.

Lipar, M., Webb, J.A., 2014. Middle–Late Pleistocene and Holocene chronostratigraphy and climate history of the Tamala Limestone, Cooloongup and Safety Bay Sands, Nambung National Park, southwestern Western Australia. Aust. J. Earth Sci. 61, 1023–1039. https://doi.org/10.1080/08120099.2014.966322.

Love, A.J., Herczeg, A.L., Leaney, F.W., Stadter, M.F., Dighton, J.C., Armstrong, D., 1994. Groundwater residence time and paleohydrology in the Otway Basin, South Australia: ^{2}H, ^{18}O and ^{14}C data. J. Hydrol. 153, 157–187. https://doi.org/10.1016/0022-1694(94)90190-2.

May, J.-H., Preusser, F., Gliganic, L.A., 2015. Refining late Quaternary plunge pool chronologies in Australia's monsoonal 'Top End'. Quat. Geochronol. 30, 328–333. https://doi.org/10.1016/j.quageo.2015.01.008.

McFarlane, D., Stone, R., Martens, S., Thomas, J., Silberstein, R., Ali, R., et al., 2012. Climate change impacts on water yields and demands in south-western Australia. J. Hydrol. 475, 488–498. https://doi.org/10.1016/j.jhydrol.2012.05.038.

Meredith, K.T., Cendón, D.I., Hankin, S., Hollins, S.E., 2012a. Allanooka-Casuarinas groundwater dating, western Australia. Department of Water. (DoW), Western Australia.

Meredith, K., Cendón, D.I., Hollins, S., 2010. North Gnangara groundwater dating, Western Australia. The Government of Western Australia (WA), Department of Water, Western Australia.

Meredith, K.T., Cendón, D.I., Pigois, J.-P., Hollins, S.E., Jacobsen, G., 2012b. Using ^{14}C and ^{3}H to delineate a recharge 'window' into the Perth Basin aquifers, North Gnangara groundwater system, Western Australia. Sci. Total Environ. 414, 456–469. https://doi.org/10.1016/j.scitotenv.2011.10.016.

Meredith, K.T., Han, L.F., Cendón, D.I., Crawford, J., Hankin, S., Peterson, M., et al., 2018. Evolution of dissolved inorganic carbon in groundwater recharged by cyclones and groundwater age estimations using the ^{14}C statistical approach. Geochim. Cosmochim. Acta 220, 483–498. https://doi.org/10.1016/j.gca.2017.09.011.

Mohtadi, M., Oppo, D.W., Steinke, S., Stuut, J.-B.W., De Pol-Holz, R., Hebbeln, D., et al., 2011. Glacial to Holocene swings of the Australian-Indonesian monsoon. Nat. Geosci. 4, 540. https://doi.org/10.1038/ngeo1209.

Mook, W.G., van der Plicht, J., 1999. Reporting C-14 activities and concentrations' Radiocarbon. Radiocarbon 41, 227–239.

Münnich, K.-O., 1957. Messung des ^{14}C-Gehaltes von hartem Grundwasser. Naturwissenschaften 34, 32–33. https://doi.org/10.1007/BF01146093.

Nagra, G., Treble, P.C., Andersen, M.S., Bajo, P., Hellstrom, J., Baker, A., 2017. Dating stalagmites in mediterranean climates using annual trace element cycles. Scientific Reports 7, 621. https://doi.org/10.1038/s41598-017-00474-4.

Pahnke, K., Sachs, J.P., 2006. Sea surface temperatures of southern midlatitudes 0–160 kyr B.P. Paleoceanography 21 (2). https://doi.org/10.1029/2005PA001191.

Petherick, L., Bostock, H., Cohen, T.J., Fitzsimmons, K., Tibby, J., Fletcher, M.S., et al., 2013. Climatic records over the past 30 ka from temperate Australia – a synthesis from the Oz-INTIMATE workgroup. Quat. Sci. Rev. 74, 58–77. https://doi.org/10.1016/j.quascirev.2012.12.012.

Phillips, F.M., Walvoord, M.A., Small, E.E., 2013. Effects of environmental change on groundwater recharge in the desert southwest. In: Groundwater recharge in a desert environment: The southwestern United States.

Plummer, L.N., Bexfield, L.M., Anderholm, S.K., Sanford, W.E., Busenberg, E., 2004. Hydrochemical tracers in the middle Rio Grande Basin, USA: 1. Conceptualization of groundwater flow. Hydrogeol. J. 12, 359–388. https://doi.org/10.1007/s10040-004-0324-6.

Plummer, L.N., Glynn, P.D., 2013. Radiocarbon dating in groundwater systems. In: IAEA (Ed.), Isotope methods for dating old groundwater. International Atomic Energy Agency, Vienna.

Raidla, V., Pärn, J., Schloemer, S., Aeschbach, W., Czuppon, G., Ivask, J., et al., 2019. Origin and formation of methane in groundwater of glacial origin from the Cambrian-Vendian aquifer system in Estonia. Geochim. Cosmochim. Acta 251, 247–264. https://doi.org/10.1016/j.gca.2019.02.029.

Reeves, J.M., Barrows, T.T., Cohen, T.J., Kiem, A.S., Bostock, H.C., Fitzsimmons, K.E., et al., 2013. Climate variability over the last 35,000 years recorded in marine and terrestrial archives in the Australian region: an OZ-INTIMATE compilation. Quat. Sci. Rev. 74, 21–34. https://doi.org/10.1016/j.quascirev.2013.01.001.

Reimer, P.J., Bard, E., Bayliss, A., Beck, J.W., Blackwell, P.G., Ramsey, C.B., et al., 2004. IntCal13 and Marine13 radiocarbon age calibration curves 0–50,000 years cal BP. Radiocarbon 55, 1869–1887. https://doi.org/10.2458/azu_js_rc.55.16947.

Rozanski, K., Johnsen, S.J., Schotterer, U., Thompson, L.G., 1997. Reconstruction of past climates from stable isotope records of palaeo-precipitation preserved in continental archives. Hydrolog. Sci. J. 42, 725–745. https://doi.org/10.1080/02626669709492069.

Salomons, W., Mook, W.G., 1986. Chapter 6 - Isotope geochemistry of carbonates in the weathering zone. In: Fritz, P., Fontes, J.C. (Eds.), Handbook of environmental isotope geochemistry, Volume 2: The terrestrial environment, B. Elsevier, Amsterdam, pp. 239–269.

Schafer, D., Johnson, S., Kern, A., 2008. Hydrogeology of the Leederville aquifer in the western Busselton-Capel groundwater area. Department of Water, Perth, Western Australia.

Shulmeister, J., Goodwin, I., Renwick, J., Harle, K., Armand, L., McGlone, M.S., et al., 2004. The Southern Hemisphere westerlies in the Australasian sector over the last glacial cycle: A synthesis. Quat. Int. 118–119, 23–53. https://doi.org/10.1016/S1040-6182(03)00129-0.

Sniderman, J.M.K., Hellstrom, J., Woodhead, J.D., Drysdale, R.N., Bajo, P., Archer, M., et al., 2019. Vegetation and climate change in Southwestern Australia during the last glacial maximum. Geophys. Res. Lett. 46, 1709–1720. https://doi.org/10.1029/2018GL080832.

Strategen, 2004. South west Yarragadee-Blackwood groundwater area water study report. Report prepared for the Water and Rivers Commission, Western Australia.

Stuiver, M., Reimer, P.J., Bard, E., Beck, J.W., Burr, G.S., Hughen, K.A., et al., 1998. INTCAL98 radiocarbon age calibration, 24,000–0 cal BP. Radiocarbon 40, 1041–1083. https://doi.org/10.1017/S0033822200019123.

Sturman, A.P., Tapper, N.J., 2006. The weather and climate of Australia and New Zealand. Oxford University Press.

Taylor, R.G., Scanlon, B., Döll, P., Rodell, M., van Beek, R., Wada, Y., et al., 2012. Ground water and climate change. Nat. Clim. Chang. 3, 322. https://doi.org/10.1038/nclimate1744.

Thorpe, P.M., 1992. Isotope hydrogeology of the confined aquifers in the southern Perth Basin, Western Australia. Hydrogeology Report No. 1992/28. Geological Survey, Western Australia.

Thorpe, P.M., Baddock, L., 1994. Groundwater resources of the Busselton-Walpole region. Hydrogeology Report No. 1994/29. Geological Survey, Perth, Western Australia.

Thorpe, P.M., Davidson, W.A., 1990. Groundwater age and hydrodynamics of the confined aquifers, Perth, Western Australia. International Conference on Grounwater in Large Sedimentary Basins, Perth, Western Australia.

Treble, P., Chappell, J.K, Gagan, M., McKeegan, K., Mark Harrison, T., 2005a. In situ measurement of seasonal δ^{18}O variations and analysis of isotopic trends in a modern speleothem from southwest Australia. Earth Planet. Sci. Lett. 233, 17–32. https://doi.org/10.1016/j.epsl.2005.02.013.

Treble, P.C., Baker, A., Ayliffe, L.K., Cohen, T.J., Hellstrom, J.C., Gagan, M.K., et al., 2017. Hydroclimate of the Last Glacial Maximum and deglaciation in southern Australia's arid margin interpreted from speleothem records (23–15 ka). Clim. Past 13, 667–687. https://doi.org/10.5194/cp-13-667-2017.

Treble, P.C., Budd, W.F., Hope, P.K., Rustomji, P.K., 2005b. Synoptic-scale climate patterns associated with rainfall δ^{18}O in southern Australia. J. Hydrol. 302, 270–282. https://doi.org/10.1016/j.jhydrol.2004.07.003.

Turner, J., Dighton, J., 2008. South West WA Leederville aquifer groundwater resources – groundwater dating – Final Report. Science Report 17/08. CSIRO Land and Water, Western Australia.

Wyrwoll, K.H., Dong, B., Valdes, P., 2000. On the position of southern hemisphere westerlies at the Last Glacial Maximum: An outline of AGCM simulation results and evaluation of their implications. Quat. Sci. Rev. 19, 881–898. https://doi.org/10.1016/S0277-3791(99)00047-5.