Using ^{14}C and ^{3}H to delineate a recharge 'window' into the Perth Basin aquifers, North Gnangara groundwater system, Western Australia

Karina Meredith [a],*, Dioni I. Cendón [a], Jon-Philippe Pigois [b], Suzanne Hollins [a], Geraldine Jacobsen [a]

[a] Australian Nuclear Science and Technology Organisation, Institute for Environmental Research, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia [b] Department of Water, PO Box K822 Perth WA 6842, Australia

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a b s t r a c t

The Gnangara Mound and the underlying Perth Basin aquifers are the largest source of groundwater for the southwest of Australia, supplying between 35 and 50% of Perth's potable water (2009–2010). However, declining health of wetlands on the Mound coupled with the reduction in groundwater levels from increased irrigation demands and drier climatic conditions means this resource is experiencing increased pressures. The northern Gnangara is an area where the Yarragadee aquifer occurs at shallow depths (~50 m) and is in direct contact with the superficial aquifer, suggesting the possibility of direct recharge into a generally confined aquifer. Environmental isotopes (^{14}C and ^{3}H) and hydrochemical modelling were used to assess the presence of a recharge 'window' as well as understand the groundwater residence time within different aquifers. Forty-nine groundwater samples were collected from depths ranging from 11 to 311 m below ground surface. The isotopic variation observed in the superficial aquifer was found to be controlled by the different lithologies present, i.e. quartz-rich Bassendean Sand and carbonate-rich sediments of the Ascot Formation. Rainfall recharge into the Bassendean Sand inherits its dissolved inorganic carbon from the soil CO_2. Organic matter throughout the soil profile is degraded by oxidation leading to anoxic/acidic groundwater, which if in contact with the Ascot Formation leads to enhanced dissolution of carbonates. Hydrochemical mass balance modelling showed that carbonate dissolution could contribute 1–2 mmol kg^{-1} of carbon to groundwaters recharged through the Ascot Formation. The corrected groundwater residence times of the Yarragadee aquifer in the northern part of the study area ranged from 23 to 35 ka, while waters in the southeastern corner ranged from sub-modern to 2 ka. Groundwater ages increase with distance radiating from the recharge 'window'. This study delineates a recharge 'window' into the commonly presumed confined aquifers of the Perth Basin, highlighting the need for appropriate sustainable management.

competition for this limited water resource. The reduction in groundwater levels identified in recent years (Yesertener, 2005) has led to the

The Gnangara Mound and the underlying generally confined aquifers of the Perth Basin (otherwise known as the Gnangara groundwater system) cover an area of approximately 2200 km^2 and constitute the largest utilised source of groundwater in the southwest of Australia. These aquifers supplied between 35 and 50% of Perth's potable water (110–152 hm^3) in the years 2009 to 2010 (Water Corporation, 2010). Groundwater from this vast system supports agriculture, industry and private domestic use. The Gnangara Mound also sustains significant groundwater dependent ecosystems, that carry social, cultural and environmental values (Clark and Horwitz, 2005; Froend et al., 2004). In addition to environmental requirements, increasing irrigation demands and urban development have resulted in strong

1 . Introduction

∗ Corresponding author.
   E-mail address: kmj@ansto.gov.au (K. Meredith).

acidification of Gnangara, Jandabup and Mariginiup Lakes and overall declining health of wetlands on the Mound (Sommer and Horwitz, 2009).

Overall, the reductions in water levels have been attributed to a combination of excessive groundwater abstraction and climate change. Groundwater levels in the Gnangara Mound (i.e. the superficial aquifer) show rapid response to rainfall and have declined systematically over the past ~40 years with variation dependent on location and land use. Salama et al. (2002) found water levels began to fall in 1975, and by 1998 water levels had dropped by 6 m in the central, 2 m in the south and 2–3 m in the northern areas of the Mound. Hydrograph data for the northern Gnangara groundwater system show a decline in water levels between: 2–7 m in the superficial, 3–10 m in the Leederville and 9–19 m in the Yarragadee aquifers since 1973 to present. With rainfall records showing a decline in average rainfall trends beginning in the early 1930s, it has been hypothesised that increasingly warmer and drier climatic conditions have influenced recharge rates to this system leading to decreasing water levels (Appleyard and Cook, 2009). Rainfall recharge estimates using various methods, and considering different land cover scenarios, have ranged from 7 to 40% (Bestow (1971); Sharma et al. (1991)) of rainfall.

There is a need to better understand the hydraulic connection between the aquifers contained within the Gnangara groundwater system. In the northern section, the Yarragadee aquifer occurs at shallow depths (~50 m) and is in direct contact with the superficial aquifer (Pigois, 2011) providing an area in the Perth Basin where groundwater recharge may occur. In this area, it was found that the groundwater models such as the Perth Regional Aquifer Modelling System (PRAMS) could not be well calibrated and that further investigations were needed. In various studies around the world, the use of radioisotopes such as tritium (^{3}H) and radiocarbon (^{14}C) has proven extremely useful in showing the connectivity or lack thereof, as well as in identifying the presence of modern recharge (Cartwright et al., 2010; Le Gal La Salle et al., 2001; Zongyu et al., 2005; amongst many others). Such an approach was considered for this study to greatly improve understanding

of the localised hydraulic complexities across the Gnangara groundwater system.

Dating groundwater using ^{14}C typically has a low temporal resolution. This can be improved by accounting for all the hydrochemical and physical processes that are likely to influence the carbon chemistry of a groundwater sample (Aranvena et al., 1995; Cartwright et al., 2010; Clark and Fritz, 1997; Gillon et al., 2009, amongst others). Previous studies of the central and southwestern section of theGnangara groundwater system have utilised radiocarbon dating methods (Thorpe and Davidson, 1991; Salama, 2005). However, the results from these studies provided interpretations based on uncorrected radiocarbon ages. The use of uncorrected radiocarbon ages in the Gnangara groundwater system can be problematic because carbonate-rich units such as the Ascot Formation (lower section of the superficial aquifer) have the potential to contribute 'dead' carbon to the groundwater sample in areas where hydraulic connection exists. The input of Dissolved Inorganic Carbon (DIC) will influence the measured radiocarbon ages and thus the hydrologeological models that rely on this data for calibration.

The purpose of this hydrochemical and isotopic groundwater investigation is to: a) delineate a recharge 'window' into the Perth Basin aquifers, as suggested by geological interpretations b) obtain representative groundwater residence times in the unstudied northern Gnangara groundwater system c) identify the major hydrogeochemical process taking place during groundwater recharge in the study area, as well as the implication of each process on groundwater residence time determinations and d) improve on current understanding of groundwater resources in the Gnangara groundwater system.

2. Environmental setting

2.1. Study site

The study site is situated in the northeastern section of the Gnangara Mound near Gingin, approximately 70 km north of Perth within the Swan Coastal Plain. The Gnangara Mound covers approximately 2200 km^2 and represents a distinct groundwater flow system contained within unconfined superficial aquifers (Davidson, 1995). Groundwater flows from an area of elevated dunes, which form the crest of the mound, towards the coast (Fig. 1). The Gnangara groundwater system has 4 aquifers; superficial, Mirrabooka (mostly to the south and east of Gnangara), Leederville, and Yarragadee.

Rivers and estuaries form the boundaries of the flow system (Appleyard and Cook, 2009). The Gingin and Moondah Brooks drain westward off the Gingin Scarp and join the Moore River towards the coast (Fig. 1). The predominant outcropping unit across the site is the Bassendean Sand dune system. Land use includes horticulture, pasture and native vegetation and there are significant wetlands in the area including the Yeal Lake, Gingin and Lennard Brooks (Yu, 2006).

The region has a Mediterranean climate with distinct hot dry summers, and mild wet winter seasons. Rainfall is highly variable with more than 80% falling during winter and spring months (Sharma and Hughes, 1985). The area has a long term average rainfall (1889−2010) of 728 mm year^{-1} and pan evaporation of 2200 mm year^{-1} (Gingin station number 9018). The 20 year moving average shows a decline in rainfall from the early 1930s, with the short term average for the period 1990−2010 dropping to 646 mm year^{-1} (Fig. 2).

2.2. Hydrogeology

The three main aquifer systems present in the study site include the unconfined superficial aquifer and the generally confined Leederville and Yarragadee aquifers from the Perth Basin. The hydrogeology of the localised study site is discussed below. However, for a more comprehensive review of the hydrogeology of the entire Perth Basin the reader is referred to Davidson and Yu (2006). The complete stratigraphic sequence and generalised hydrogeology for the site is presented in Table 1 (reproduced from Pigois, 2011) and again later in the discussion section (Fig. 10). A subcrop map at the base of the superficial formations shows that in the study area, the Pinjar Member is absent from the Leederville Formation and that the Parmelia Group and Yarragadee Formations are in contact with the superficial formations in the southeast (Fig. 3). The distribution of the geologic formations means that the aquifers in the area are potentially hydraulically connected and recharge of the Leederville and Yarragadee aquifers may be occurring.

The superficial aquifer forms a multilayered, unconfined aquifer with an average thickness of ~50 m. Hydraulic conductivities in this unit are relatively high, ranging from 10 to 50 m day^{-1} with an average of 15 m day^{-1} (Davidson and Yu, 2006). The sediments comprising the superficial aquifer range from clayey (Guildford Clay) in the north and east, to predominantly sand (Bassendean Sand) in the centre, to sand and limestone (Tamala Limestone) to the northwest of the study area. The Ascot Formation lies at the base of the superficial aquifer and comprises mostly sand and limestone with some minor clay. The Ascot Formation ranges from absent in (NG03 and NG09) to 29 m in thickness and has an average hydraulic conductivity of 8−10 m day^{-1} (Davidson and Yu, 2006). The water table is located at the top of the superficial aquifer and is referred to as the Gnangara Mound. Groundwater flow direction generally follows the topography and runs east to west (Fig. 1). The

sandy nature of the Bassendean Sand and common solution cavities of the Ascot Formation are expected to allow a good hydraulic connection with underlying aquifers in the absence of confining layers. Major losses from the superficial aquifer are through evaporation/transpiration, groundwater abstraction (Salama et al., 2005) and through hydraulic connection with the deeper aquifer where confining units are absent. Groundwater recharge to the superficial aquifer occurs via direct rainfall infiltration and thus is highly dependent on rainfall variability.

The Leederville aquifer is generally a major confined aquifer in the Perth Basin. However, in the study area it is unconfined due to the absence of the Pinjar Member, and consists of interbedded sands and clays of the Wanneroo and Mariginiup Members reaching a maximum thickness of about 200 m. The Leederville aquifer is not continuous to the Gingin Scarp and stops where the Yarragadee Formation and Parmelia Group subcrop the superficial formations (Fig. 3). Groundwater flow in the Leederville aquifer is generally from east to west in the study area (Tuffs, 2011) and is hydraulically connected to the flow system within the superficial aquifer. To the west of the area, upward hydraulic head indicates discharge to the superficial aquifer (site NG12), but mostly downward hydraulic gradients ranging from 0.16 to 12 m suggesting recharge from the superficial aquifer (Pigois, 2011).
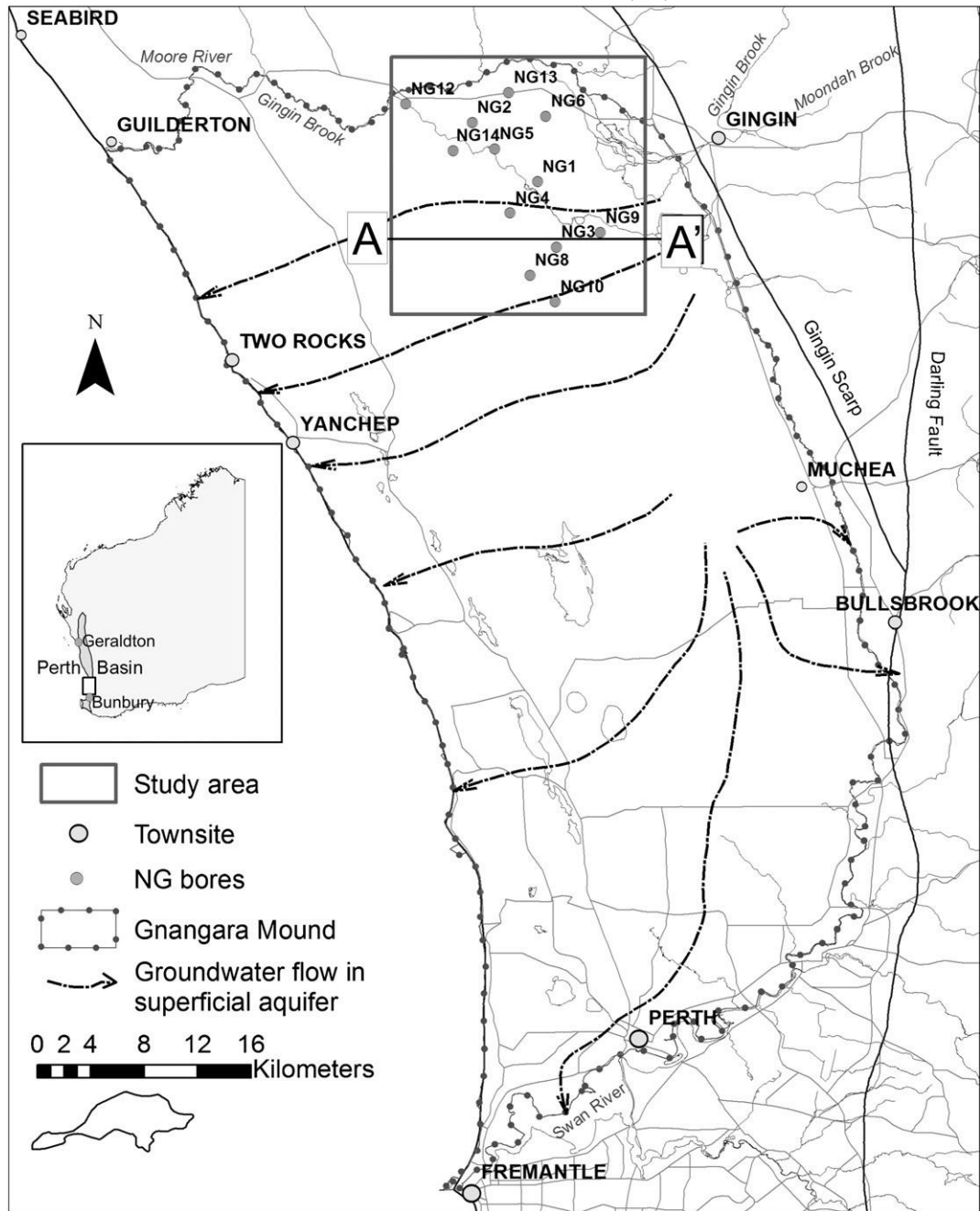
Fig. 1. Location map of the North Gnangara Mound study area with well locations (NG bores) and generalised groundwater flow direction for the superficial aquifer in Gnangara Mound.

Adapted from Davidson and Yu (2006) in relation to the Perth Basin.

The Yarragadee Formation is approximately 3000 m thick, and together with the Gage Formation forms the Yarragadee aquifer which is the most widespread aquifer in the Perth Basin and it is mostly confined. The aquifer is divided into a northern flow system (where the study area is located), extending from Geraldton to Southern Perth, and a southern flow system from Bunbury to the South Coast known as the southwest Yarragadee (Commander, 2009). In most areas across the study site, the Leederville aquifer overlies the Yarragadee aquifer and is locally confined by the Mariginiup and South Perth Shale aquitards. The Yarragadee aquifer consists mostly of coarse grained quartz sand and clayey sand with some sandy clay and clay bands. Groundwater flow in the Yarragadee is generally to the southwest (Davidson, 1995) and the vertical hydraulic gradient in the north Gnangara area is about 0.15 to 19 m lower than the Leederville and superficial aquifers suggesting recharge by downward leakage (Pigois, 2011).

3. Methodology

3.1. Groundwater sampling and field treatment

From April to May 2009, forty-nine groundwater samples were collected from nested wells at the twelve sites throughout the study area (Fig. 3). These wells were installed from August 2007 to November
2008 to depths that ranged from 11 to 311 m bgs. Screen length were 3 m long in the shallow wells (b50 m) and 6 m long in the deeper wells (>50 m). Monitoring wells were completed within one target aquifer. Prior to sampling, wells were developed and standing water levels were measured from the top of the casing. Based
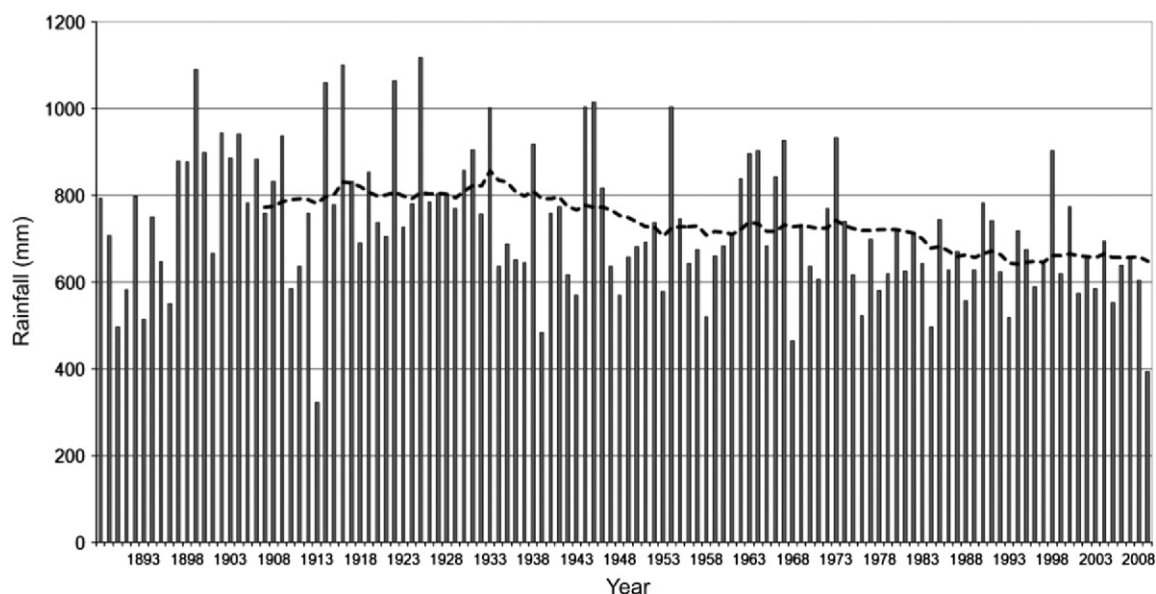

Fig. 2. Rainfall data from Gingin (1889–2010). The dotted black line represents the 20 year moving average.

on sampling depths, different pumping methods were employed to obtain representative samples. Deeper wells >150 m bgs were generally sampled using low flow methods (Puls and Barcelona, 1996). Shallower wells had at least three well-volumes removed with stabilisation of field parameters prior to sampling. Field parameters included: Specific Conductivity (SC), Oxidation-Reduction Potential (ORP), Dissolved Oxygen (DO), temperature and pH.

Groundwater samples were collected from an in-line, 0.45 μm, high volume filter. Total alkalinity concentrations were determined in the

Table 1
Stratigraphic sequence and generalised hydrogeology for the site, including the maximum thickness and lithological description for each unit (Pigois, 2011).

Age	Stratigraphy	Maximum Thickness (m)	Lithology and environment of deposition	Aquifer
Quaternary —	Superficial Formations	62		
Neogene	Tamala Limestone	30	Limestone and calcarenite with minor sand and clay	Superficial aquifer
	Bassendean Sand	53	Fine- to medium-grained quartz sand with discontinuous ferruginised horizons	Superficial aquifer
	Guildford Clay	14	Sandy silt and clay, ferruginised horizons	Local aquitard
	Ascot Formation	29	Mostly limestone with sand and minor clay	Superficial aquifer
Cretaceous	Leederville Formation	198		
	Wanneroo Member	175	Sand beds (up to 30 m thick) separated by clay horizons; fluvial	Leederville aquifer

	Mariginiup Member	23	Finely interbedded clay, silt and sand layers; fluvial	Leederville aquifer
	South Perth Shale	21	Clay and silt with minor sand horizons	Confining bed
	Gage Formation	44	Sand, silt and clay; fluvial with minor marine	Yarragadee aquifer
Jurassic	Parmelia Group	38	Silt, clay and sand	Local confining beds
	Yarragadee Formation	258	Sand, silt and clay; fluvial with minor marine	Yarragadee aquifer

field by acid–base titration using a HACH digital titrator. The Fe^{2+} concentration was determined using a portable colourimeter (HACH DR/ 890). Samples for anions were collected in 125 mL (High Density Polyethylene) bottles, with no further treatment. Samples for cations were collected in 125 mL HDPE bottles and acidified with nitric acid (HNO_3). The $\delta^{13}C_{DIC}$ samples were collected in conditioned 12 mL glass vials (Exetainers) with no head space. Samples for ^{14}C and ^3H analysis were collected in 1 L Nalgene HDPE bottles and were sealed with tape to eliminate atmospheric exchange during storage.

3.2. Groundwater analysis

The chemical composition of water samples was analysed at Australian Nuclear Science and Technology Organisation (ANSTO) by inductively coupled plasma-atomic emission spectroscopy for cations and ion chromatography for anions. Cation and anion results were assessed for accuracy by evaluating the charge balance error percentage (Freeze and Cherry, 1979) and most samples fell within ±5% except sample NG8D which was −9%. The $\delta^{13}C_{DIC}$ values were analysed by liberating CO_2 from each sample and injecting it into a helium stream, which was separated from other gases by gas chromatography attached to a Finnigan 252 mass spectrometer using a Conflo III. Results were reported as per mil (‰ VPDB) deviation from the international carbonate standard, NBS19 with a precision of ±0.1‰.

The ^3H and ^{14}C samples were analysed at ANSTO. For ^3H analysis, water samples were distilled and electrolytically enriched prior to being analysed by liquid scintillation method. The ^3H concentrations were expressed in tritium units (TU) with an uncertainty of ±0.1 TU and quantification limit of 0.4 TU. Tritium was measured by counting beta decay events in a liquid scintillation counter. A 10 mL sample distillate was mixed with the scintillation compound that releases a photon when struck by a beta particle. Photomultiplier tubes in the counter convert the photons to electrical pulses that are counted over 51 cycles for 20 min.

For ^{14}C analysis, the total DIC was processed into CO_2 by acidifying the samples with H_3PO_4 and extracting the liberated CO_2 gas using a custom built extraction line. The CO_2 sample was then heated in a sealed glass tube, containing baked CuO and Ag and Cu wire, at 600 °C for 2 h to remove any sulphur compounds that may have been liberated from the groundwater sample during the CO_2 extraction. The CO_2 sample was then converted into graphite by reducing it with excess hydrogen gas in the presence of an iron catalyst at 600 °C.
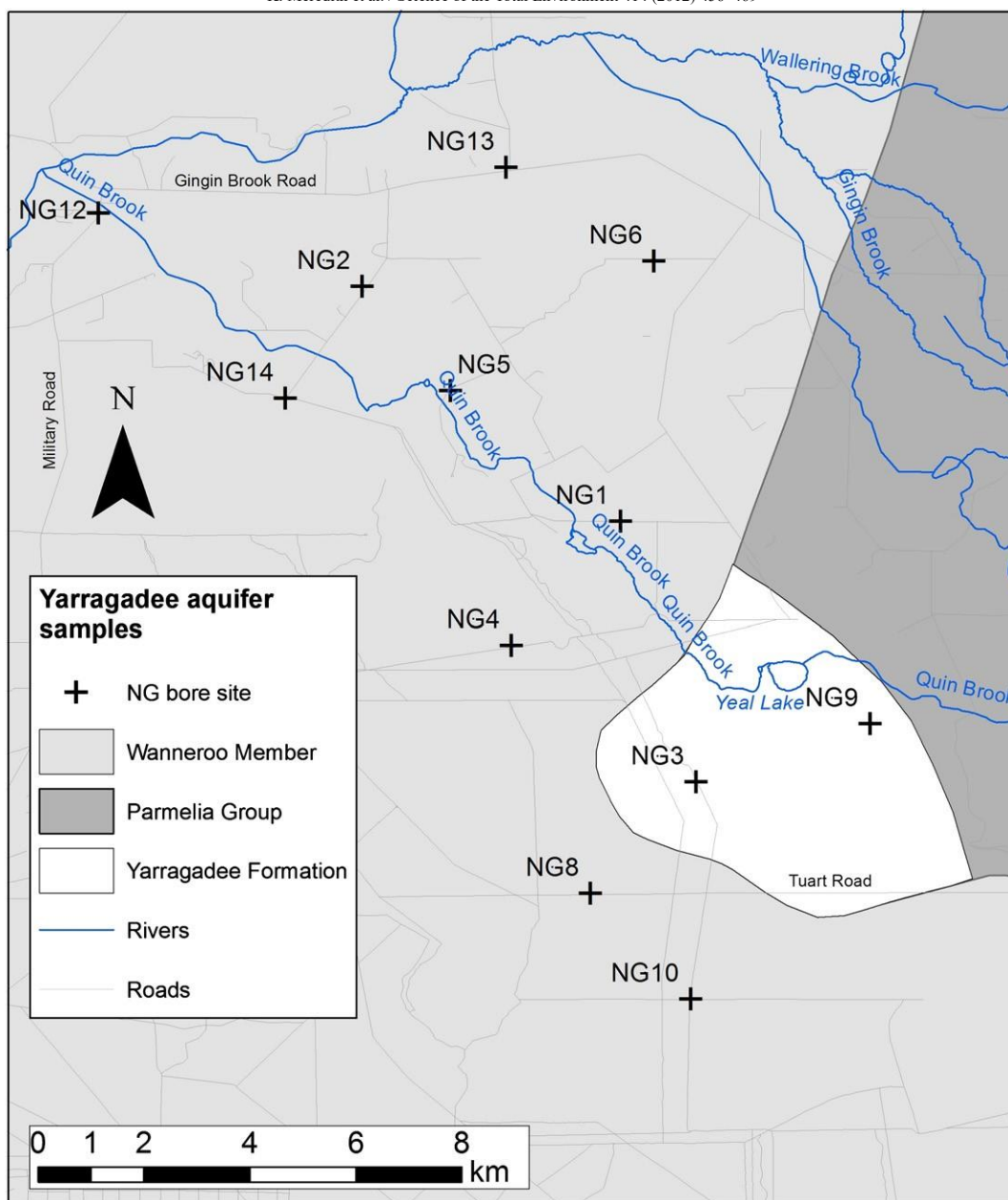
Fig. 3. Subcrop at the base of the superficial formations (Pigois, 2011).

The ^{14}C activities were measured by accelerator mass spectrometry using the ANSTO 2MV tandetron accelerator, STAR (Fink et al., 2004). The ^{14}C results were reported as percent Modern Carbon (pMC) with an average 1σ error of ±0.3 pMC. Radiocarbon age calculations were performed following the methods outlined in Stuiver and Polach (1977). The uncorrected ages quoted are 'conventional radiocarbon ages' (years Before Present) and not calendar ages. This method assumes that atmospheric ^{14}C levels have been constant in the past and uses a half-life of 5568 years. All ^{14}C measurements were normalised against the oxalic acid (HOXI) international standard. This method assumes that atmospheric ^{14}C levels have been constant in the past and that isotopic fractionation of all sample activities is accounted for by normalising $\delta^{13}C$ to −25‰, relative to PDB (Stuiver and Polach, 1977).

Saturation indices for carbonates, the partial pressure of CO_2 (pCO_2), HCO_3^- and CO_3^{2-} concentrations were calculated using the WATEQ4F thermodynamic database in the PHREEQC 2.4.2 programme (Parkhurst and Appelo, 1999).

4. Results

Groundwaters for this study were sampled from various aquifers within the Gnangara Mound and underlying Perth Basin aquifers. The three main aquifer systems present include the superficial, Leederville and Yarragadee aquifers. This study focuses on the northern part of the Gnangara groundwater system where the Yarragadee aquifer occurs at shallow depths (~50 m) and is in direct contact with the superficial aquifer (Pigois, 2011). For simplicity, the Leederville and Yarragadee aquifers will be collectively termed as the Perth Basin aquifers.

The major ion chemistry highlights the hydrochemical variability of groundwaters from the different aquifers or lithologies within the study site. Shallow groundwater samples (b50 m bgs) from the superficial aquifer ranged from fresh (Total Dissolved Solids (TDS)= 114 mg L^{−1}) to brackish (TDS=1826 mg L^{−1}) but were generally fresh (average: TDS=548 mg L^{−1}). The quartz-rich lithologies of the Bassendean Sand (superficial aquifer) were Na–Cl-rich waters (Fig. 4). $Ca^{2+}+Mg^{2+}/HCO_3^-$ ratios for shallow groundwaters from the quartz-rich sand varied with depth with the highest values (4.0 and 5.3) at shallow depths (Table 2).

Groundwaters that were abstracted from carbonate-rich lithologies, such as the Ascot Formation (lowest part of superficial aquifer) were Ca–HCO$_3$-rich waters (Fig. 4) with an average value of 0.7 for Ca^{2+}+Mg^{2+}/HCO$_3^-$ ratios. A bivariate plot of Ca^{2+}+Mg^{2+} vs. HCO$_3^-$ (not shown) indicated that most groundwaters from the carbonate-rich unit (i.e. the Ascot Formation) plotted on either the 1:1 or 1:2 line, implying carbonate dissolution. Groundwaters of the Perth Basin aquifers were also found to be relatively fresh with an average TDS of 575 mg L^{-1} for the Leederville and 623 mg L^{-1} for the Yarragadee groundwaters. Na$^+$/Cl$^-$ ratios of groundwaters from the study site were close to unity with an average of 0.97 (Table 2).

The groundwaters of the superficial aquifer show the greatest variation in δ^{13}C$_{DIC}$ signatures. Groundwaters from the Bassendean Sand (superficial aquifer) had an average δ^{13}C$_{DIC}$ of −22.8‰ (n=13) and the Ascot Formation (lower superficial aquifer) an average of −12.2‰ (n=10). A similar range in δ^{13}C$_{DIC}$ variation was found in groundwaters elsewhere in the Perth Basin [−9.3 to −20.5‰] (Fig. 5) with an average value of −15.8‰ (n=25). The ^{14}C activities in the superficial aquifer were found to range from 8.6 to 97.6 pMC (Fig. 5a) [average=61.3 pMC: n=21]. In the Perth Basin aquifers, values ranged from 1.1 to 84.3 pMC [average=32.9 pMC: n=25]. Of the 34 samples analysed for ^{3}H, 20 samples did not contain any measurable ^{3}H above the quantification limit of 0.1 TU (Fig. 5b), which indicates they are likely to be >60 years old. Most of the groundwaters with no measured ^{3}H were from the Perth Basin aquifers. Groundwaters residing in the Bassendean Sand were found to contain ^{3}H with an average activity of 0.8 TU (n=13). Groundwater in the Ascot Formation was generally below detection limit but sample NG14D did have a relatively elevated reading of 1.2 TU.

5. Discussion

Various environmental isotopes (δ^{13}C, ^{14}C and ^{3}H) as well as hydrochemical parameters were used to understand the hydrochemical evolution and hence residence times of groundwaters contained within different aquifers of the northern Gnangara groundwater system. Conceptual hydrochemical models are presented and have been evaluated using mass balance modelling, giving us a greater understanding of the evolution of carbon from rainfall recharge to the observed groundwater sample. For this paper, mass balance modelling solutions were validated with chemical speciation modelling, geologic data, environmental isotopes and conceptual hydrogeological models, as recommended by Kalin (1999)

5.1. Conceptual hydrochemical models

The hydrochemical evolution of groundwater into the north Gnangara groundwater system is considered according to two recharge scenarios. The first recharge scenario is where the Ascot Formation (lower superficial aquifer) is present at the base of the superficial formations (Fig. 6a). The second recharge scenario is where the Bassendean Sand (superficial aquifer) directly overlies the Perth Basin aquifers and the carbonate-rich unit of the Ascot Formation is absent (Fig. 6b). Understanding the hydrochemical evolution of each recharge scenario is important for identifying hydrochemical processes that are likely to influence carbon and subsequently groundwater residence times.
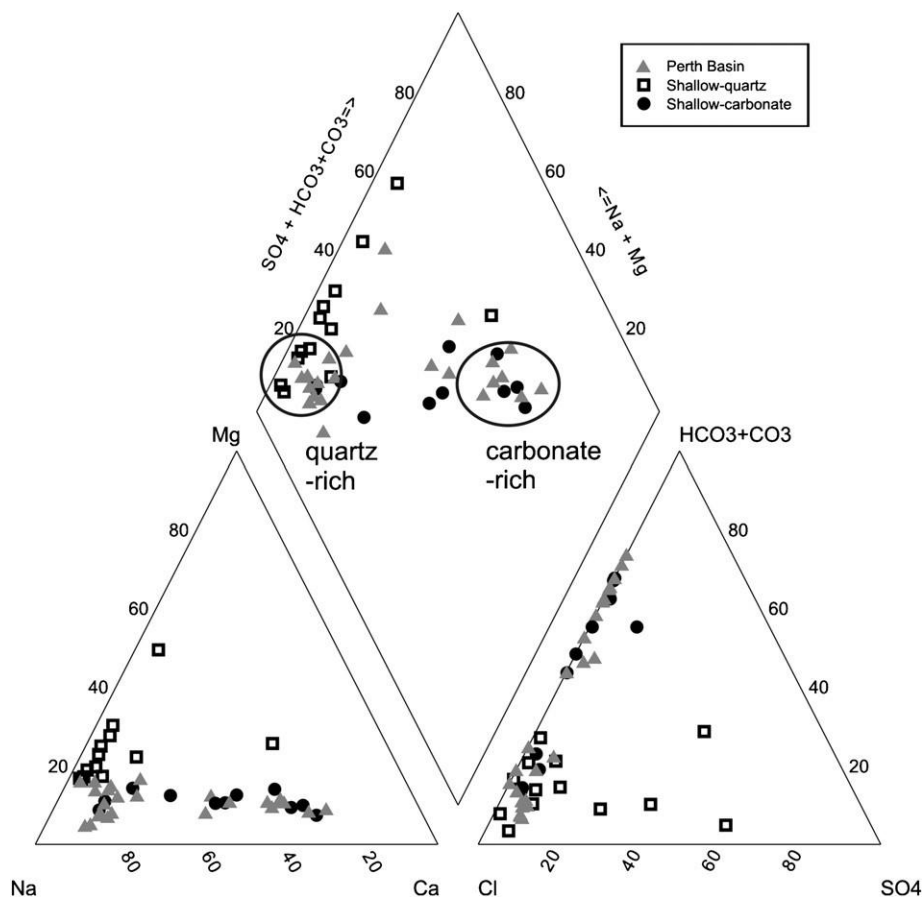

Fig. 4. Piper diagram of groundwaters from the superficial (shallow-quartz = Bassendean Sands and shallow-carbonate = Ascot Formation), Perth Basin (Leederville and Yarragadee) aquifers.

Table 2

Chemical composition, $\delta^{13}C_{DIC}$, and saturation indices for calcite (SI$_{Cal}$) of groundwater samples (Carb = carbonate-rich aquifer, Qtz = Qtz-rich aquifer and Perth = Perth Basin aquifers).

ID	Geology	Aquifer	Depth	T	pH	Na	Ca	Mg	K	Cl	SO$_4$	HCO$_3$	SiO$_2$	$\delta^{13}C$	SI$_{Cal}$
			m bgs	°C		mmol L^{-1}	mmol L^{-1}	mmol L^{-1}	mmol L^{-1}	mmol L^{-1}	mmol L^{-1}	mmol L^{-1}	mmol L^{-1}	‰	
NG01C	Ascot	Carb	46	19.6	7.2	1.48	1.58	0.25	0.10	1.64	0.000	3.42	0.14	−8.97	−0.20
NG02B	Ascot	Carb	41	21.0	7.2	3.96	1.73	0.44	0.10	4.43	0.006	3.43	0.13	−9.64	−0.21
NG04D	Ascot	Carb	50	18.9	6.8	1.33	1.65	0.18	0.10	1.49	0.000	3.04	0.17	−10.64	−0.60
NG05C	Ascot	Carb	45	21.0	7.1	4.13	2.06	0.59	0.10	5.13	0.000	4.81	0.15	−10.77	−0.10
NG06C	Ascot	Carb	38	27.9	7.5	22.44	1.70	1.58	0.34	23.67	0.542	3.87	0.19	−13.67	0.17
NG06D	Ascot	Carb	18	21.0	7.4	20.70	1.48	1.12	0.36	20.87	0.469	3.66	0.25	−13.11	−0.11
NG10C	Ascot	Carb	53	19.4	6.5	1.14	1.06	0.17	0.06	1.24	0.026	2.14	0.08	−11.62	−1.25
NG12B	Ascot	Carb	33	24.9	6.8	8.92	1.10	0.93	0.34	10.38	0.385	2.61	0.24	−14.16	−0.89
NG12C	Tamala	Carb	8	22.1	7.3	3.68	1.45	0.38	0.12	3.05	0.020	3.81	0.17	−14.56	−0.10
NG13C	Ascot	Carb	44	17.0	6.8	7.18	1.62	0.74	0.19	8.83	0.167	2.74	0.19	−17.28	−0.81
NG14D	Ascot	Carb	47	20.8	7.0	2.09	1.62	0.44	0.04	1.95	0.344	3.25	0.07	−11.76	−0.37
NG01A	Yarragadee	Perth	272	23.3	7.0	4.35	0.29	0.14	0.18	2.48	0.135	2.50	0.13	−14.79	−1.25
NG01B	Leederville	Perth	109	25.1	5.8	3.38	0.31	0.15	0.21	3.27	0.177	1.05	0.29	−20.51	−2.70
NG02A	Leederville	Perth	107	22.6	6.6	13.05	1.82	1.19	0.48	17.60	0.698	1.50	0.18	−15.88	−1.17
NG03A	Yarragadee	Perth	226	18.4	6.5	1.67	0.60	0.13	0.27	1.21	0.000	1.98	0.15	−16.12	−1.55
NG03B	Yarragadee	Perth	138	18.7	5.6	1.26	0.09	0.12	0.13	1.27	0.001	0.42	0.17	−19.93	−3.90
NG04A	Yarragadee	Perth	272	28.0	7.2	12.74	1.24	0.67	0.40	11.68	0.375	2.92	0.13	−15.36	−0.36
NG04B	Yarragadee	Perth	167	20.9	7.0	2.07	0.96	0.24	0.18	2.14	0.000	2.40	0.13	−18.54	−0.72
NG04C	Leederville	Perth	110	22.0	7.0	2.07	1.78	0.34	0.12	2.20	0.000	4.18	0.14	−9.31	−0.26
NG05A	Yarragadee	Perth	294	22.0	6.9	19.31	1.43	0.90	0.49	20.11	0.781	1.83	0.12	−16.00	−0.91
NG05B	Leederville	Perth	85	21.8	6.1	2.88	0.39	0.37	0.23	2.74	0.002	2.15	0.23	−16.64	−2.01
NG06A	Yarragadee	Perth	293	21.2	7.7	16.44	0.96	0.47	0.47	16.39	0.281	2.64	0.11	−14.75	−0.12
NG06B	Leederville	Perth	118	24.8	5.3	2.83	0.06	0.28	0.16	3.13	0.115	0.36	0.18	−20.49	−4.38
NG08A	Yarragadee	Perth	260	19.5	7.2	1.24	1.02	0.22	0.11	1.13	0.000	2.81	0.13	−14.85	−0.45
NG08B	Gage	Perth	172	19.4	7.0	1.07	0.86	0.17	0.09	1.16	0.000	1.94	0.12	−14.46	−0.82
NG08C	Leederville	Perth	111	23.2	7.3	1.06	1.55	0.21	0.09	1.18	0.000	3.32	0.12	−11.78	−0.03
NG09A	Yarragadee	Perth	299	26.7	5.5	2.64	0.20	0.27	0.23	3.22	0.000	0.75	0.32	−15.23	−3.26
NG09B	Yarragadee	Perth	145	21.0	5.7	2.94	0.13	0.31	0.15	3.19	0.001	0.59	0.22	−17.01	−3.53
NG10A	Yarragadee	Perth	303	20.7	6.9	1.35	0.96	0.20	0.15	1.27	0.001	2.36	0.12	−16.38	−0.86
NG10B	Leederville	Perth	91	19.9	6.9	1.07	1.23	0.16	0.08	1.16	0.000	2.44	0.12	−12.86	−0.70
NG12A	Leederville	Perth	102	23.8	6.4	10.53	0.54	0.93	0.46	12.35	0.542	1.51	0.18	−17.02	−1.88
NG13A	Leederville	Perth	170	21.5	6.9	14.79	1.14	0.74	0.47	15.96	0.510	2.11	0.22	−16.99	−0.98
NG13B	Leederville	Perth	99	21.6	6.9	3.45	1.29	0.43	0.21	3.58	0.104	3.30	0.27	−16.16	−0.56
NG14A	Yarragadee	Perth	303	25.7	6.9	12.88	1.26	1.08	0.65	15.54	0.583	2.16	0.13	−17.73	−0.82
NG14B	Leederville	Perth	214	19.9	6.6	16.66	1.28	1.14	0.50	18.17	0.802	1.44	0.14	−16.41	−1.38
NG14 C	Leederville	Perth	87	22.7	7.1	2.82	2.10	0.37	0.10	3.13	0.003	4.42	0.14	−9.78	−0.04
NG01D	Bassendean	Qtz	19	19.4	5.8	3.11	0.34	0.54	0.12	3.98	0.055	1.07	0.18	−20.00	−2.71
NG02C	Bassendean	Qtz	14	20.5	5.8	0.97	0.79	0.44	0.05	0.96	0.677	0.93	0.09	−18.18	−2.41
NG03C	Bassendean	Qtz	47	19.7	5.0	1.30	0.03	0.14	0.05	1.44	0.004	0.29	0.08	−23.63	−5.14
NG03D	Bassendean	Qtz	13	19.7	4.8	1.70	0.06	0.35	0.04	1.30	0.469	0.25	0.06	−24.15	−5.09
NG04E	Bassendean	Qtz	8	19.3	4.1	1.33	0.03	0.16	0.03	1.41	0.072	0.18	0.05	−21.68	−6.22
NG05D	Bassendean	Qtz	16	20.3	5.4	3.94	0.06	0.41	0.05	4.15	0.034	0.35	0.19	−22.83	−4.38
NG08D	Bassendean	Qtz	44	18.9	5.8	1.30	0.07	0.15	0.06	1.55	0.021	0.59	0.10	−20.56	−3.67

| NG08E | Bassendean | Qtz | 14 | 19.1 | 5.3 | 1.67 | 0.11 | 0.93 | 0.05 | 1.47 | 1.198 | 0.20 | 0.08 | −23.96 | −4.57 |
NG09C	Bassendean	Qtz	46	19.8	5.1	4.31	0.11	0.75	0.08	4.85	0.438	0.97	0.09	−24.31	−3.96
NG09D	Bassendean	Qtz	20	19.9	4.0	2.61	0.09	0.34	0.09	2.93	0.135	0.52	0.04	−24.23	−5.47
NG10D	Bassendean	Qtz	13	19.1	5.0	2.19	0.07	0.51	0.04	2.37	0.469	0.32	0.06	−23.00	−4.73
NG13D	Bassendean	Qtz	15	20.4	5.3	21.49	0.63	3.37	0.19	27.02	0.865	1.00	0.84	−22.81	−3.20
NG14E	Bassendean	Qtz	17	21.0	5.0	2.58	0.05	0.26	0.04	2.54	0.156	0.77	0.07	−24.25	−4.45
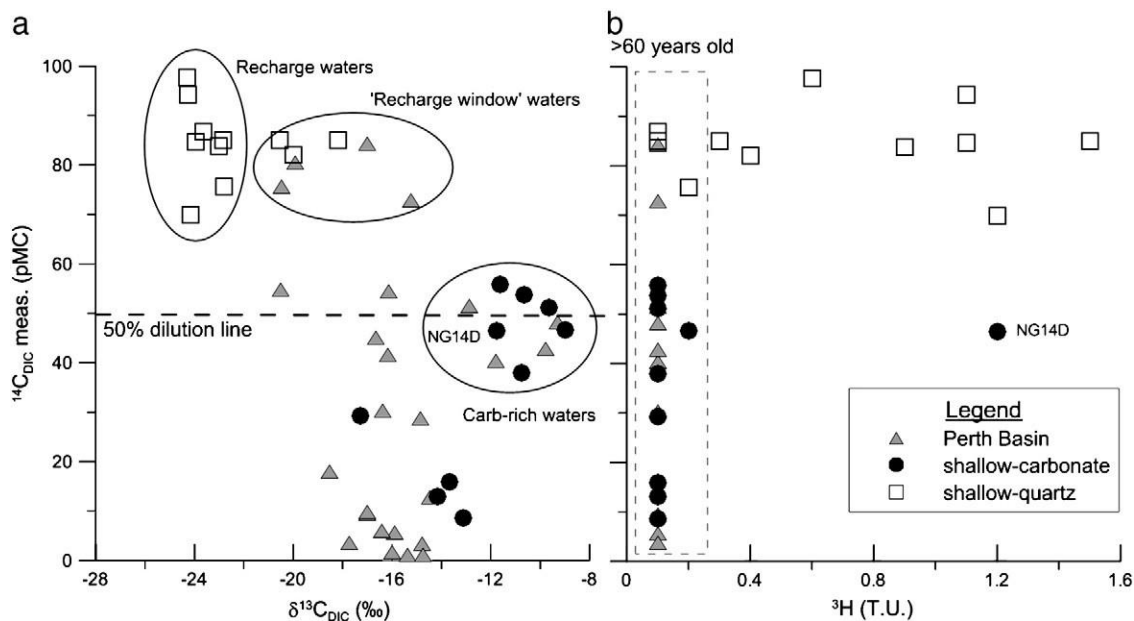
Fig. 5. Bivariate plots of measured ^{14}C activity vs. (a) $\delta^{13}C_{DIC}$ and (b) ^3H activity. Groundwaters will plot on the 50% dilution line if DIC is contributed from calcite dissolution.

5.1.1. Rainfall recharge in the Bassendean Sand

Groundwaters are generally recharged into the Bassendean Sand (superficial aquifer) from rainfall across the site. The hydrochemistry of these groundwaters are anoxic, acidic and can have elevated iron, sulphide and Dissolved Organic Carbon (DOC) concentrations (Turner and Yesertener, 2009). Bekele (2005) reported DOC concentrations (n=108) throughout the superficial aquifer generally below 8 mg L^{-1} with some samples reaching up to 72 mg L^{-1}. Although the present study does not report DOC concentrations, the general parameters and hydrochemistry observed in our study are similar to these waters.

Once rainfall is recharged as groundwater into the Bassendean Sand the groundwater inherits a $\delta^{13}C_{DIC}$ (Fig. 5a), which is similar to the signature of soil zone CO$_2$ (i.e. ~25‰: Clark and Fritz, 1997). This assumption is validated by an average $\delta^{13}C_{DIC}$ of −22.8‰ for Bassendean Sand groundwaters. Depleted $\delta^{13}C_{DIC}$ signatures indicate that the vegetation that forms the DOC in the soil zone follows a C$_3$ photosynthetic pathway (Tipple and Pagani, 2007). Groundwater in the Bassendean Sand (i.e. shallow qtz-sand aquifer) also had higher measured ^{14}C activities (70 to ~100 pMC) than other groundwater in the study area (Fig. 5a) indicating it is exchanging with the ^{14}C active soil zone, and is open to modern carbon.

The anoxic condition produced in these shallow groundwaters within the Bassendean Sand is likely to occur from the decay of organic matter (CH$_2$O) via oxidation according to the following reaction:

$$CH_2O + O_2 \rightarrow H_2O + CO_2$$
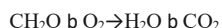
The CH$_2$O is located on the surface and throughout the soil profile. Additional evidence for high organic matter compositions comes from work completed in the podzolic soils of the Gnangara Mound (Gerritse et al., 1996). These authors found that surface soils generally contained elevated organic contents of about 10 g kg^{-1}.

Oxidation of DOC initially takes place by aerobic bacteria (Clark and Fritz, 1997) and all the available oxygen is consumed. Evidence
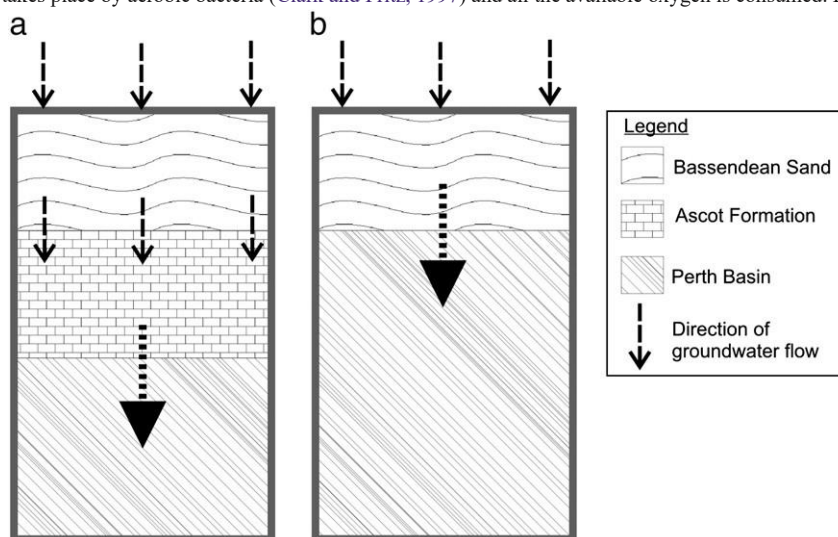

Fig. 6. Diagram of the different stages of groundwater recharge into the Perth Basin aquifers through (a) the Bassendean Sand (superficial aquifer) and then into the Ascot Formation (lowest part of the superficial aquifer) and (b) the Bassendean Sand.
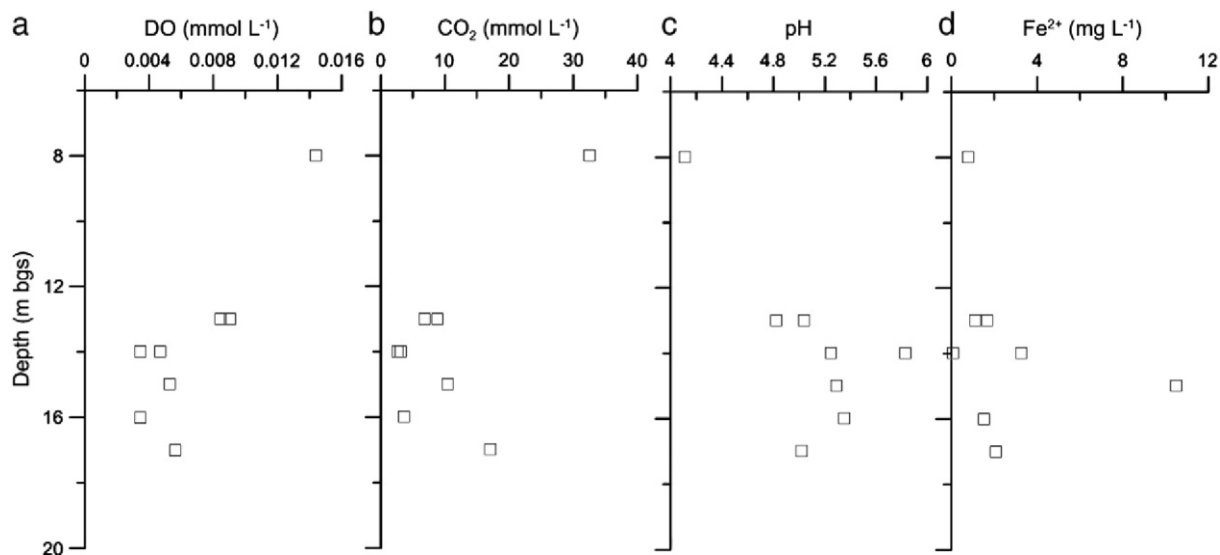
Fig. 7. Bivariate plots of depth vs. (a) Dissolved oxygen, (b) CO₂, (c) pH and (d) Fe²⁺ for groundwaters abstracted from the top ~20 m of Bassendean Sand.

of this process is observed in the Bassendean Sand with a steep decrease in DO concentration with depth in the upper (top 20 m) section of the aquifer (Fig. 7a). The production of carbonic acid or hydrated CO_2 through this oxidation reaction is also evident with the elevated CO_2 concentration in the shallowest groundwater sample and remains fairly high throughout the aquifer profile (Fig. 7b). The pH of the Bassendean Sand groundwaters initially decreases due to the increase in CO_2 concentration. However, as the groundwater migrates deeper through the sandy aquifer, the pH increases slightly but generally remains fairly low suggesting CH_2O degradation throughout the profile (Fig. 7c).

Because the groundwaters of the Bassendean Sand are strongly influenced by redox reactions, the presence of other electron acceptors (besides oxygen) must be considered so that sound mass balance models can be developed for this system. As the available oxygen is consumed in the aquifer (as seen with a decrease in DO with depth (Fig. 7a)), other electron acceptors are needed to mediate the oxidation of CH_2O as groundwater migrates deeper in the aquifer. The reduction of MnO_2 and NO_3^- was investigated because these electron acceptors yield higher energy for the bacteria during reduction. The pH and Eh diagrams for manganese indicate that Mn^{2+} and $MnCO_3$ would be the likely phases (Appelo and Postma, 2005). Groundwaters from the Bassendean Sand have low Mn concentrations (b3.6×10⁻³ mmol L⁻¹). If the reduction of MnO_2 was an important process, high Mn concentration would result, therefore this process can be discounted. Nitrate concentrations in the Bassendean Sand groundwaters are low ranging from below detection limit to 1.4×10⁻² mmol L⁻¹ indicating while minor concentration of nitrate is present, the reduction of nitrate is not likely to be a dominant process. The next electron acceptor considered was Fe-oxyhydroxides and if they are present in the system they may mediate these reactions. These minerals can be found as coatings on the sand grains within the Bassendean Sand (Wilson and Garcia, 2009) and would liberate Fe^{2+} according to the following reaction:

$$CH_2O \text{ þ } 4FeOOH \text{ þ } 7H^{þ} \rightarrow 4^{Fe_{2}þ} \text{ þ } HCO_3^{-} \text{ þ } 6H_2O:$$
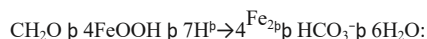
The presence of elevated concentrations of Fe^{2+} also provides further evidence of this reaction (Fig. 7d). Sulphate reduction may also be taking place, however the generally lowsulphide and much higher sulphate concentrations suggest this process is not important. This reduces the possibility of more advanced reduction processes such as methanogenesis taking place.

To evaluate the validity of these proposed hydrochemical processes, net transfer models (Plummer et al., 1994) were applied to groundwater sampled from the Bassendean Sand. Hydrogeochemical models were constructed using Ca, Na, C, Fe, Cl and redox as constraints. The modelled phases were organic matter (CH_2O), $CO_{2(g)}$, ferric hydroxide, NaCl (from atmospheric sources), Ca/Na exchange and calcite. A hypothetical rainwater chemistry (Appelo and Postma, 2005) was used as the initial water. Modelling was based on the assumption that piston flow recharge is occurring in this system and that the groundwater system is at chemical steady state.

Carbon mass balance using Rayleigh distillation equations for all incoming carbon sources and all isotopically fractionating outgoing carbon phases were calculated (Plummer et al., 1994). Models were assessed for accuracy by comparing the observed and computed $\delta^{13}C$ results produced by each model ($\delta^{13}C$ values ±1‰). Because a valid mass balance model must calculate a $\delta^{13}C$ value similar to the observed, models that failed to predict this $\delta^{13}C$ value were not used in the interpretation. This approach was taken for all hydrochemical modelling.

A representative model for the Bassendean Sand (NG02C) calculated that approximately 0.3 mmol kg⁻¹ of CH_2O is oxidised, 3 mmol kg⁻¹ of CO_2 resulted from in-gassing from the soil zone or organic matter degradation, 0.8 mmol kg⁻¹ of calcite is dissolved, 1 mmol kg⁻¹ of NaCl is incorporated from atmospheric sources and small amounts of FeOOH dissolution (0.01 mmol kg⁻¹) were leading to the observed ion concentrations.

Modelling supports the hypothesis that redox reactions control the evolution of shallow Bassendean Sand groundwaters with CH_2O oxidation as the major contributor of carbon. The low pH values observed in the Bassendean Sand groundwater (pH 4–5.8) indicate that the aqueous carbon species will be in the form of CO_2. Low concentrations of Ca, HCO_3^- (average: 0.1 and 0.6 mmol L⁻¹, respectively), depleted $\delta^{13}C_{DIC}$ values (average: −22.6‰) and groundwater that is undersaturated with respect to calcite and dolomite indicates that carbonate dissolution is not the major process influencing carbon evolution in the Bassendean Sand.

5.1.2. Hydrochemical evolution from Bassendean Sand to the Ascot Formation

Once the groundwater has migrated through the Bassendean Sand (superficial aquifer), it is generally recharged into the carbonate-rich aquifer of the Ascot Formation (lower superficial aquifer), and a shift in groundwater chemistry becomes evident (Fig. 8). The dissolution of carbonate is the most likely explanation of this distinct change in
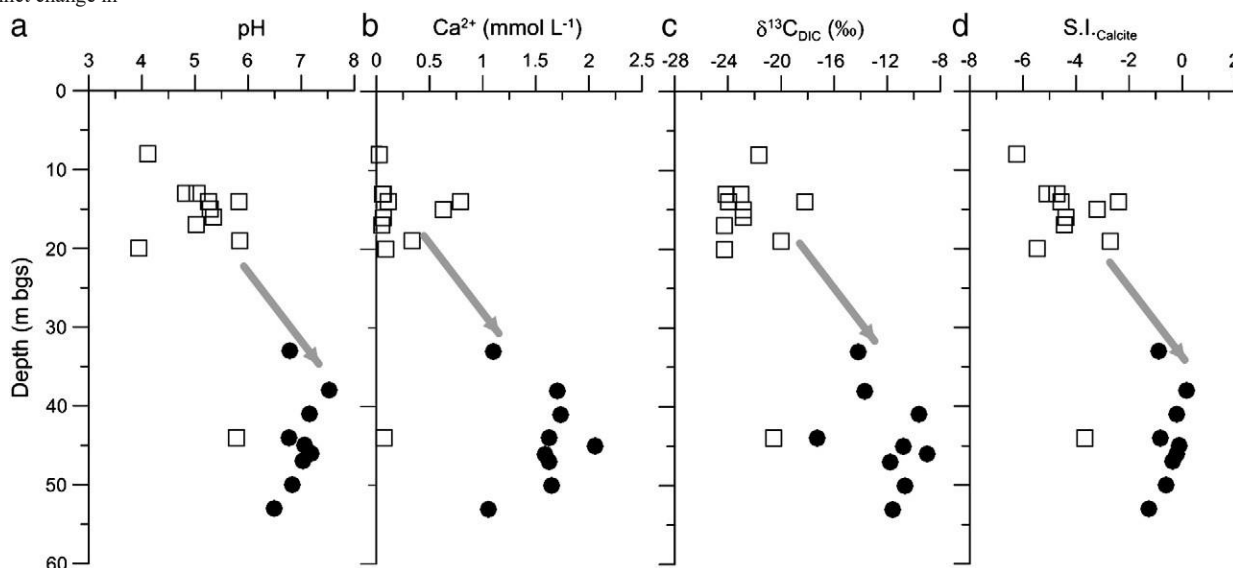

Fig. 8. Bivariate plots of depth vs. (a) pH (b) Ca^{2+} (c) $\delta^{13}C_{DIC}$ and (d) saturation indices for calcite for groundwaters from the top ~60 m of the study area. Arrows indicate the increase in parameters between the Bassendean Sand (□) and Ascot Formation (●).

chemistry. Groundwater infiltrating through carbonate-rich lithologies can have up to 50% of its HCO_3^- contributed from a 'dead' carbon source (Tamers, 1975) according to the following reaction:

$$CaCO_3 + H_2O + CO_2 \frac{1}{4} Ca_{2+} + 2HCO_3^-:$$

The majority of the carbonate-rich groundwaters from the Ascot Formation plot around the 50% dilution line due to this reaction (Fig. 5a). Therefore, measured radiocarbon results from the Ascot Formation are considered not to be representative ages if not corrected for this influx.

Groundwaters from the Bassendean Sand contain high concentrations of CO_2 liberated from the oxidation of CH_2O. This acidic recharge is likely to enhance the weathering of carbonate minerals in the Ascot Formation. Once the recharging waters encounter the carbonate unit, the dissolution of carbonate minerals leads to an increase in pH, Ca^{2+} concentration and enrichment in $\delta^{13}C_{DIC}$ values (Fig. 8). The $\delta^{13}C_{DIC}$ values ranged from −17.3 to −9.0 with an average of −12.8‰ (n=7), while $\delta^{13}C$ of carbonates (n=2) have an enriched signature with an average $\delta^{13}C$ value of −1.0‰ in the top 25 m of the profile. This indicates that inorganic carbon is most likely contributed from the dissolution of carbonates. Enriched $\delta^{13}C_{DIC}$ values would be expected if methane degassing was contributing carbon to the groundwaters as seen in Leybourne et al. (2006). Groundwaters also move towards carbonate saturation as indicated by an increase in calcite saturation implying a shift from open to closed system conditions (Fig. 8d). The development of secondary porosity in the form of solution cavities in the Ascot Formation is likely and would explain the observed low uncorrected ^{14}C activities (46.5 pMC) but elevated ^3H (1.2 TU) for sample NG14D located in the Ascot Formation. Tritium data confirms that most groundwaters from the Ascot Formation are older than the overlying Bassendean Sand.

Mass balance modelling was used to quantify the amount of carbon contributed from carbonate dissolution into the groundwater sample. Hydrogeochemical models for this aquifer were constructed using Ca, Na, C, Fe, Cl, S and redox as constraints. The modelled phases were CH_2O, $CO_{2(g)}$, ferric hydroxide (goethite), pyrite, NaCl, calcite and Ca/Na exchange. Initial waters were assigned according to the following criteria: if a shallower Bassendean Sand groundwater from the same site existed then this water was assigned, if it did not or models did not produce acceptable $\delta^{13}C$ values, sample NG02C was assigned as the initial water (see Table 3). A representative model for the Ascot Formation (i.e. NG02C to NG02B) calculated that 1.4 mmol kg^{-1} was incorporated from the dissolution of carbonates, very little CH_2O oxidised (0.02 mmol kg^{-1}), FeOOH dissolved (0.06 mmol kg^{-1}), in-gassing of CO_2 (0.02 mmol kg^{-1}), and 3.4 mmol kg^{-1} of NaCl is dissolved during the evolution of a Bassendean Sand groundwater to an Ascot Formation groundwater. Modelling results indicate the majority of carbon within a groundwater sample is contributed from carbonate dissolution in the Ascot Formation.

5.2. Radiocarbon correction modelling

The oxidation of CH_2O was found to be the main processes contributing modern carbon to Bassendean Sand (superficial aquifer) groundwaters and carbon evolution occurred under open-system conditions. However, once the groundwater migrated into the Ascot Formation (lower superficial aquifer), closed-system conditions dominated the hydrochemical evolution of the groundwater and carbonate dissolution became the main contributor of carbon. The Ascot Formation represents a source of 'dead' (^{14}C-free) carbon to infiltrating water, which can reduce the ^{14}C activity and lead to erroneous radiocarbon ages.

A number of geochemical models can be applied to account for sinks and sources of ^{14}C (see Clark and Fritz (1997) for a detailed description). In this study two different methods of radiocarbon corrections were implemented and compared to determine ^{14}C dilution: A) A chemical correction based on the initial and final DIC (Tamers, 1975) and B) A matrix exchange correction that takes into account cation concentrations and isotope mass balances to quantify dead-^{14}C contributions (Fontes and Garnier 1979). These models, generally applied on a single-well, were compared with mass transport models constructed in NETPATH (Plummer et al., 1994),

based on the geochemical reactions presented in Section 5.1. NETPATH calculates mass transfer between an initial and final well adjusting the initial ^{14}C and accounting for all the sources and sinks of carbon along the chosen flow path. A more detailed description of this modelling approach can be found in Aranvena et al. (1995) and Plummer and Sprinkle (2001). Models that computed δ^{13}C values within ±2‰ were considered and the total age was recorded. However if models did not produce δ^{13}C values comparable to measured values, single-well models were used.

5.2.1. Carbonate values and modelling assumptions

An evaluation of whether the various units of the superficial aquifer contained carbonates was made based on (1) regional geology (Davidson, 1995) (2) local observations during drilling (Pigois, 2009)

Table 3

Summary of uncorrected and corrected radiocarbon ages (BS = Bassendean Sand, TL = Tamala Limestone, AF = Ascot Formation, LF = Leederville Formation, YF = Yarragadee Formation, GF = Gage Formation, M = modern (b0.06 ka) and SM = sub-modern (>0.06 but b1 ka)). *Final ages were calculated by either single-well, NETPATH correction methods or whether ^{3}H was contained in the sample. NETPATH final ages were calculated step-wise i.e. Initial water NG03A (2 ka)→NG01A (23–26 ka)=final age of 25–28 ka for NG01A.

ID	Unit	Depth	^{3}H	^{14}C	Age	Age_ Tamers	Age_F-G	ID	ID	$^{13}C_{comp}$	$^{13}C_{obs}$	Age_ Tamers	Age_F-G	*Age
				Uncorrected		Single-well		Netpath						Final
		m bgs	TU	pMC	ka	ka	ka	Initial	Final	‰	‰	ka	ka	ka
NG01A	YF	272		3.4	27.2	23.7	24.6	NG03A	NG01A	−12.9	−14.8	24.2	23.1	25–28
NG01B	LF	109		54.8	4.8	3.9	4.1	NG03B	NG01B	−19.8	−20.5	4.0	2.9	3–4
NG01C	AF	46	0.2	46.6	6.1	1.5	0.0	NG01D	NG01C	−10.5	−9	2.1	1.1	1–2
NG01D	BS	19	0.4	82.1	1.6	0.6	0.5	Rain	NG01D	−24.5	−20	1.1	0.9	SM
NG02A	LF	107	0.1	5.6	23.2	20.5	21.0	Not recharged from the unit above						21
NG02B	AF	41	0.1	51.1	5.4	0.8	0.0	NG02C	NG02B	−10.9	−9.6	1.7	0.0	SM-2
NG02C	BS	14	1.5	84.9	1.3	0.3	0.0	Rain	NG02C	−19.2	−18.2	0.0	0.0	M
NG03A	YF	226		54.4	4.9	2.3	2.1	NG03B	NG03A	−20.5	−16.1	1.0	0.0	2
NG03B	YF	138		80.5	1.7	1.2	0.6	NG02C	NG03B	−18.2	−19.9	0.7	0.0	SM
NG03C	BS	47	0.1	86.8	1.1	1.0	1.6	Rain	NG03C	−24.6	−23.6	0.8	0.6	SM
NG03D	BS	13	1.2	69.9	2.9	2.8	3.7	Rain	NG03D	−23.9	−24.2	2.5	2.4	M-3
NG04A	YF	272		1.2	35.6	31.7	34.0	Not recharged from the unit above						32–34
NG04B	YF	167		18.0	13.8	9.8	13.6	NG03B	NG04B	Model did not run				10–14
NG04C	LF	110	0.1	48.2	5.9	1.7	0.0	NG04D	NG04C −13		−9.3	2.9	0.2	SM-2
NG04D	AF	50	0.1	53.8	5.0	1.2	0.0	NG04E	NG04D −6.6		−10.6	4.3	3.0	SM-1
NG04E	BS	8	1.4	Not analysed										M
NG05A	YF	294		1.6	33.0	29.7	31.6	Not recharged from the unit above						30–32
NG05B	LF	85		45.1	6.4	4.7	3.9	Not recharged from the unit above						4–5
NG05C	AF	45	0.1	37.9	7.8	3.5	1.7	NG02C	NG05C −14.1 −10.8			4.7	3.1	2–4
NG05D	BS	16	0.3	84.9	1.3	1.0	1.5	Rain	NG05D −24.3 −22.8			0.8	0.5	SM
NG06A	YF	293		1.1	36.2	31.9	34.5	Not recharged from the unit above						32–35
NG06B	LF	118		75.6	2.3	1.9	1.3	Not recharged from the unit above						1–2
NG06C	AF	38	0.1	15.9	14.8	9.9	11.4	Not recharged from the unit above						10–11
NG06D	AF	18	0.1	8.6	19.7	15.0	15.9	Not recharged from the unit above						16–18
NG08A	YF	260		28.7	10.0	5.6	7.4	NG03A	NG08A −13.9 −14.9			6.9	5.8	6–9
NG08B	GF	172		12.8	16.5	12.6	13.5	Not recharged from the unit above						13–14
NG08C	LF	111	0.1	40.3	7.3	2.5	2.0	NG10C	NG08C	−12.9	−11.8	2.6	0.0	SM-3
NG08D	BS	44	0.1	84.9	1.3	0.4	0.4	NG08E	NG08D	−24.8	−20.5	0.9	0.9	SM
NG08E	BS	14	1.1	84.6	1.4	1.1	2.1	Rain	NG08E	−22	−24	0.0	0.0	M
NG09A	YF	299	0.1	72.9	2.5	2.0	0.0	NG09B	NG09A	−19.9	−15.2	2.0	0.5	SM-2
NG09B	YF	145	0.1	84.3	1.4	0.7	0.0	NG02C	NG09B	−17.9	−18.2	0.2	0.0	SM
NG09C	BS	46	0.6	97.6	0.2	0.0	1.1	NG09D	NG09C	−25.3	−24.3	0.1	0.0	M
NG09D	BS	20	1.3	Not analysed										M
NG10A	YF	303	0.1	30.3	9.6	5.8	7.7	NG03A	NG10A	−14.3	−16.3	6.7	5.6	8–9
NG10B	LF	91	0.1	51.6	5.3	1.3	0.6	NG10C	NG10B	−10.4	−12.9	2.1	0.0	SM-1
NG10C	AF	53	0.1	55.8	4.7	2.0	0.0	NG02C	NG10C	−13.5	−11.6	1.9	0.1	SM-2
NG10D	BS	13	0.9	83.8	1.4	1.3	1.6	Rain	NG10D	−24.6	−23	1.1	1.0	M-1
NG12A	LF	102	0.1	9.5	18.9	16.9	17.0	Not recharged from the unit above						17
NG12B	AF	33	0.1	13.0	16.4	12.9	12.8	NG12C	NG12B	−18.1	−14.2	13.2	13.4	13
NG12C	TL	8	0.3	41.6	7.0	2.3	4.1	Rain	NG12C	−5.3	−14.6	0.0	0.0	SM

NG13A	LF	170		9.9	18.6	15.0	17.4	NG13B	NG13A	−16.4	−17	14.9	15.6	19–21
NG13B	LF	99		41.5	7.1	3.0	5.0	NG13C	NG13B	−15.5	−16.2	2.4	3.2	4–5
NG13C	AF	44	0.1	29.2	9.9	1.9	2.4	NG02C	NG13C	−15	−17.3	8.1	6.3	2
NG13D	BS	15	0.2	75.7	2.2	1.9	2.4	Rain	NG13D	−26.3	−22.8	2.0	2.0	2
NG14A	YF	303	0.1	3.7	26.6	23.1	26.1	Not recharged from the unit above						23–26
NG14B	LF	214		6.0	22.7	20.0	20.9	Not recharged from the unit above						20–21
NG14C	LF	87	0.1	42.8	6.8	2.4	0.0	NG14D	NG14C	−9.4	−9.8	0.5	0.0	SM-5
NG14D	AF	47	1.2	46.5	6.2	1.9	0.8	NG14E	NG14D	−10.9	−11.8	5.1	5.0	M-5
NG14E	BS	17	1.1	94.3	0.5	0.3	1.3	Rain	NG14E	−24.7	−24.3	0.3	0.3	M-SM

and (3) X-Ray Diffraction analysis of selected drill chip samples (Meredith et al., 2010). Two sediment samples containing carbonates were analysed for $\delta^{13}C$ composition with results showing an enriched signature with an average $\delta^{13}C$ value of −1.0‰ in the top 25 m of the profile. These are typical of marine derived carbonate values (Craig, 1953). Therefore, calcite was assigned this $\delta^{13}C$ value for modelling purposes.

The carbonate units within the studied lithologies were classified as "dead" with regard to ^{14}C activity (> 50,000 years) and therefore assigned a value of 0 pMC. The studied areas, particularly the native vegetated sections, are dominated by C_3 type vegetation, therefore the $\delta^{13}C$ isotopic signal of soil CO_2 will have a value of around −25‰. Modelling assumptions for organic matter and soil $CO_{2(g)}$ were $\delta^{13}C = -25$‰ and a ^{14}C activity of 100 pMC.

5.2.2. Corrected radiocarbon ages

Radiocarbon corrections have been applied to all samples according to the main hydrogeochemical processes identified. When a defined flow path could be established, based on groundwater levels and hydrochemical evaluation, NETPATH modelling was applied. In cases where flow paths could not be established or calculated $\delta^{13}C_{DIC}$ values did not coincide with measured, a single-well correction was applied as a more robust alternative to no correction. This approach was taken for most Perth Basin aquifer groundwaters not located near the recharge 'window'. The final age was interpreted from both modelling methods and an age range presented in Table 3.

For the Bassendean Sand groundwaters, NETPATH models were considered more robust than the single-well methods because they took into account open-exchange reactions such as CH_2O oxidation, which the single-well models do not consider. However, for the Ascot Formation groundwaters, both single-well and
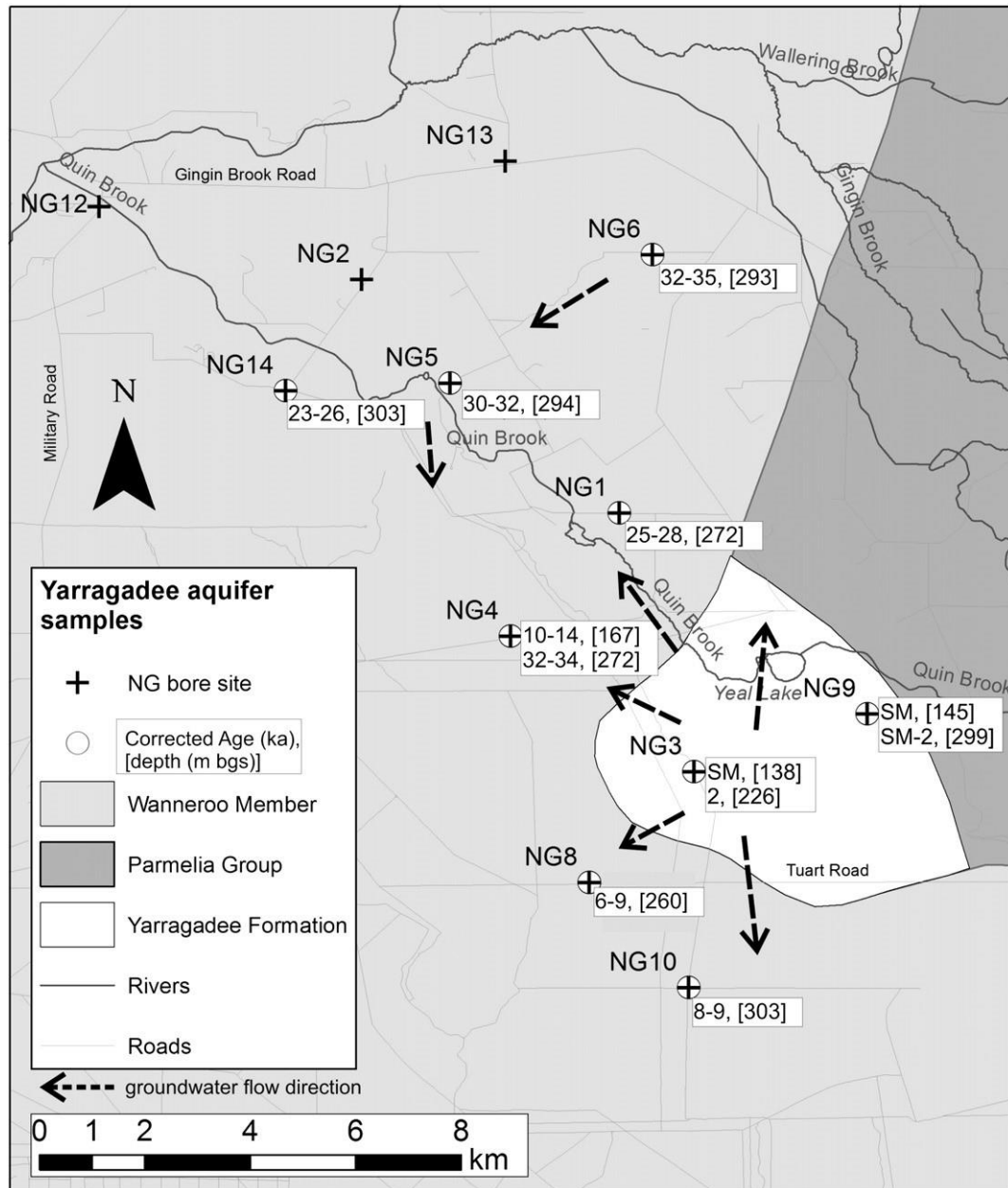

Fig. 9. Interpreted groundwater ages (ka) and sampling depths (m bgs) based on corrected radiocarbon and ^{3}H results for the Yarragadee aquifer with groundwater flow direction.

NETPATH calculated ages were used. Three NETPATH models (NG04D, NG05C and NG13C) produced higher than expected corrected ages, these models also did not converge, and consequently, the single-well corrections were used for age calculations. This is considered suitable because closed-system dissolution reactions of carbonate dominate the evolution of the groundwaters from the Ascot Formation and these single-well correction methods assume carbonate dissolution takes place under closed system conditions (Clark and Fritz, 1997). Groundwaters from the Ascot formation to the northeast (NG06D and NG06C) were unusually old waters and are not considered representative of the superficial aquifer; therefore singe-well methods were applied.

Flow paths could not be identified for most wells in the Perth Basin aquifers located away from the recharge 'window' (i.e. the hydrochemistry provided no evidence of inter-aquifer connection), hence single-well corrections were applied to these groundwaters. Groundwaters located in and around NG03 and NG09 (the area where the superficial aquifer is in direct contact with the Yarragadee aquifer) were modelled using a Bassendean Sand recharge water (NG02C) (Table 3). NETPATH models for the shallower samples (NG09B and NG03B) converged well and were found to be younger than the single-well models. Other groundwaters from the Perth Basin aquifers influenced by recharge in this area were modelled using either NG03A or NG03B as initial waters, depending on their depth.

5.3. Identifying a recharge 'window' into the Perth Basin aquifers

Geological interpretation suggests that there is a connection between the superficial and Yarragadee aquifers in the study site because the normally present confining layers are absent (Pigois, 2011). If true, this interpretation should be confirmed by geochemical observations. To assess the presence of the recharge 'window', groundwater residence times were corrected for the influx of 'dead' carbon, recharge
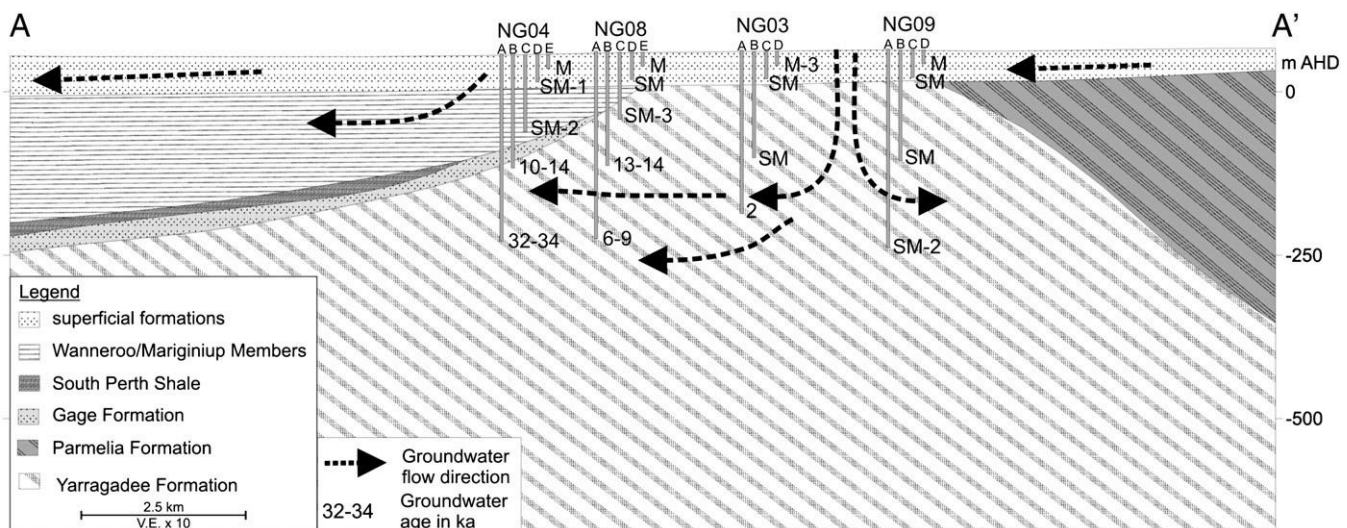
Fig. 10. Geological cross-section with corrected groundwater age and flow direction (arrows) for the study site (refer to Fig. 1 for cross section location A–A'). (M = modern (b0.06 ka) and SM = sub-modern (>0.06 but b1 ka)).

processes characterised and general groundwater flow direction determined either by direct observation (water level) or indirectly (^{14}C).

The age of groundwater from the Yarragadee aquifer in the northern part of the study area ranges from 23 to 35 ka, similar to other groundwaters in the southern section of the Yarragadee aquifer (Thorpe and Davidson, 1991). However, Yarragadee waters in the southeastern corner of the study area (NG03 and NG09) within the Yarragadee aquifer were found to be considerably younger, ranging from sub-modern (>0.06) to ~2 ka with the youngest groundwater found in NG09 near Lake Yeal (Fig. 9). Groundwater ages increase in a southerly direction towards NG08 and NG10 (~4 km from NG09) to ages between 6 and 9 ka. This trend continues to the north in the Yarragadee aquifer with water at NG04B also found to be relatively young 10−14 ka. The presence of younger waters represents the extent of fresh rainfall derived pulses originating from the recharge 'window' that includes sites NG03 and NG09 (Fig. 10).

This recharge 'window' into the Yarragadee aquifer is an area of prime interest from a water resource perspective because not only is it important that this area is left to actively recharge fresh water into the Yarragadee aquifer but it also needs to be protected from point-source contamination. For example, the application of pesticides to soils in this area would lead to a higher risk of contamination to a generally confined and hence protected groundwater resource. Identification of recharge 'windows' into the Yarragadee aquifer is important for managing water allocations and will help with calibrating hydrogeological models of the Gnangara groundwater system.

6. Conclusions

The suspected recharge 'window', suggested by geological assessment, has been validated by groundwater hydrogeochemical analysis. In the area around NG03 and NG09 near Lake Yeal, the underlying Yarragadee Formation is in direct contact with the superficial aquifer and rainfall is actively recharging the Yarragadee aquifer. Groundwater with ^{14}C activities as high as 84.3 and 72.9 pMC have been found at 145 and 299 m depth, respectively.

In order to assess groundwater residence time, hydrogeochemical processes during recharge were identified for the North Gnangara groundwater system with emphasis on the superficial aquifer around the recharge 'window'. The groundwater isotopic variation observed in the superficial aquifer was found to be controlled by the different lithologies present. The quartz-rich Bassendean Sand (superficial aquifer) was found to have evolved from rainfall recharge and is controlled by redox reactions with CH_2O oxidation as the major contributor of carbon. The low pH, Ca^{2+} and HCO_3^- concentrations, depleted $\delta^{13}C_{DIC}$ values and undersaturated with respect to carbonates indicate minimal carbon is contributed from carbonate dissolution in the Bassendean Sand. Groundwater in the Bassendean Sand has high ^{14}C activities (70 to ~100 pMC) indicating it is exchanging with the ^{14}C active soil zone, and that it is an open system to modern carbon.

Wherever the carbonate-rich sediments of the Ascot Formation are present the acidic recharge flowing from the Bassendean Sands enhances the weathering of carbonate minerals, leading to an increase in pH, Ca^{2+}, enrichment in $\delta^{13}C_{DIC}$, low ^{14}C activities (~50 pMC) and a move towards carbonate saturation. This overall shift in chemistry indicates that inorganic carbon is contributed from the dissolution of carbonates moving from an open to closed system condition.

The underlying Perth Basin aquifers had a wide range of radiocarbon ages, dependent on their position relative to the recharge 'window'. In general, groundwater ages in the Yarragadee aquifer, in the northern part of the study area, ranged from 25 to 35 ka.

It was found that no single radiocarbon correction method was successfully applicable to all the different aquifers contained in the Gnangara groundwater system. Generally, flow paths could be established between wells at different depths in the superficial aquifer, and between the superficial and Yarragadee aquifer around the recharge 'window'. This allowed the use of mass transfer models between an initial and final well. However, flow paths could not be established reliably in the northern section of the study area, where the Perth Basin aquifers are confined. In some of those cases single-well corrections were favoured over no correction. Overall, the corrected reported ages account for the major hydrogeochemical processes identified and are considered to constitute a better residence time than uncorrected values.

The identified recharge 'window' into the Yarragadee aquifer is an area of prime interest from a water resource perspective because not only is it important that this area is left to actively recharge fresh water into the Yarragadee aquifer, but it also needs to be protected from point-source contamination. Application of pesticides to soils in this area could lead to a higher risk of contamination and recharge of contaminants into an otherwise generally confined aquifer and hence protected groundwater resource. Identification of these recharge 'windows' into the Yarragadee aquifer is important for managing water allocations and will help

with calibrating hydrogeological models of the Gnangara groundwater system. The understanding of aquifer interaction in this area is crucial to sustainable management of confined aquifer abstraction in a drying climate.

Acknowledgements

References

Appelo CAJ, Postma D. Geochemistry, groundwater and pollution. Amsterdam: AA Balkema Publishers; 2005.

Appleyard S, Cook T. Reassessing the management of groundwater use from sandy aquifers: acidification and base cation depletion exacerbated by drought and groundwater withdrawal on the Gnangara Mound, Western Australia. Hydrogeol J 2009;17:579–88.

Aranvena R, Wassenaar LI, Plummer LN. Estimating ^{14}C groundwater ages in a methanogenic aquifer. Water Resour Res 1995;31. 2307–2137.

Bekele E. Compilation and assessment of water quality data for the superficial aquifer, Gnangara Mound, Western Australia. CSIRO: Water for a Healthy Country National Research Flagship; 2005.

Bestow TT. The water balance in the north Gnangara area. Western Australia Geological Survey, Annual Report 1970; 1971. p. 14–7.

Cartwright I, Weaver TR, Cendón DI, Swane I. Environmental isotopes as indicators of inter-aquifer mixing, Wimmera region, Murray Basin, Southeast Australia. Chem Geol 2010;277:214–26.

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

Clark JD, Horwitz P. Annual Report for the Wetland Macroinvertebrate Monitoring Program of the Gnangara Mound Environmental Monitoring Project — Spring 2004 to Summer 2005, report to the Department of Environment; 2005.

Commander P. New water from old sources: case study of the south-west Yarragadee aquifer. Tag Newsletter No. 151; 2009. June.

Craig H. The geochemistry of the stable carbon isotopes. Geochim Cosmochim Acta 1953;3:53–92.

Davidson WA. Hydrogeology and groundwater resources of the Perth Region, Western Australia. Geological Survey of Western Australia Bulletin, 142. ; 1995.

Davidson WA, Yu X. Perth region aquifer modelling system — PRAMS, Hydrogeology and groundwater modelling. Department of Water Hydrogeological Record Series HG 20; 2006.

Fink D, Hotchkis M, Hua Q, Jacobsen G, Smith AM, Zoppi U, et al. The ANTARES AMS facility at ANSTO. NIM B 2004;223–224:109–15.

Fontes JC, Garnier JM. Determination of the initial ^{14}C activity of the total dissolved carbon: a review of the existing models and a new approach. Water Resour Res 1979;15:399–410.

Freeze RA, Cherry JA. Groundwater. Englewood Cliffs, NJ: Prentice-Hall Inc.; 1979.

Froend RH, Rogan R, Loomes R, Horwitz P, Bamford M, Storey A. Study of ecological water requirements on the Gnangara and Jandakot mounds under Section 46 of the Environmental Protection Act. Tasks 3 & 5: Parameter Identification and Monitoring Program Review, prepared for Water and Rivers Commission, Centre for Ecosystem Management. Joondalup: Edith Cowan University; 2004.

Gerritse RG, Beltran J, Hernandez F. Adsorption of atrazine, simazine, and glyphosate in soils of the Gnangara Mound, Western Australia. Aust J Soil Res 1996;34:599–607.

Gillon M, Barbecot F, Gibert E, Corcho Alvarado JA, Marlin C, Massault M. Open to closed system transition traced through the TDIC isotopic signature at the aquifer recharge stage, implications for groundwater ^{14}C dating. Geochim Cosmochim Acta 2009;73:6488–501.

Kalin RM. Radiocarbon dating of groundwater systems. In: Cook PG, Herczeg AL, editors. Environmental tracers in subsurface hydrology. Boston: Kluwer; 1999. p. 112–44.. 1999.

Le Gal La Salle C, Marlin C, Leduc C, Taupin JD, Massault M, Favreau G. Renewal rate estimation of groundwater based on radioactive tracers (^{3}H, ^{14}C) in an unconfined aquifer in a semi-arid area, Iullemeden Basin, Niger. J Hydrol 2001;254:145–56.

Leybourne MI, Clark ID, Goodfellow WD. Stable isotope geochemistry of ground and surface waters associated with undisturbed massive sulfide deposits; constraints on origin of waters and water–rock reactions. Chem Geol 2006;231:300–25.

Meredith K, Cendón D, Hollins S. North Gnangara groundwater dating, Western Australia. A report prepared for The Government of Western Australia (WA). Department of Water; 2010. ANSTO/C-1084.

Parkhurst D, Appelo C. User's guide to PHREEQC (version 2) — a computer program for speciation, batch-reaction, one dimensional transport, and inverse geochemical calculations. Water Resour Invest Rep U.S. Geol Surv 1999;99:4259.

Pigois JP. North Gnangara bore completion report. Hydrogeological Report Series. Department of Water, Government of Western Australia; 2009. HR277.

Pigois JP. Geology and hydrogeology of the north Gnangara area. Hydrogeological Record Series. Department of Water, Government of Western Australia; 2011. p. HG55. in prep.

Plummer NL, Sprinkle CL. Radiocarbon dating of dissolved inorganic carbon in groundwater from confined parts of the Upper Floridan aquifer, Florida, USA. Hydrogeol J 2001;9:127–50.

Plummer N, Prestemon E, Parkhurst D. An interactive code (NETPATH) for modelling NET geochemical reactions along a flow PATH, Version 2.0. Technical Report Water-Resources Investigations Report 94–4169. U.S. Geological Survey; 1994.

Puls RW, Barcelona MJ. EPA ground water issue: low-flow (minimal drawdown) ground-water sampling procedures; 1996. EPA/540/S-95/504.

Salama RB. Interconnectivity between the superficial aquifer and the deep confined aquifers of the Gnangara Mound, Western Australia. Water Air Soil Pollut Focus 2005;5:27–44.

Salama RB, Bekele E, Hatton TJ, Pollock DW, Lee-Steere N. Sustainable yield of groundwater of the Gnangara Mound, Perth, Western Australia. Proceedings of an international conference on balancing the groundwater budget; 2002. 12–17 May, Darwin, IAH Australia.

Salama RB, Silberstein R, Pollock D. Soils characteristics of The Bassendean and Spearwood Sands of the Gnangara Mound (Western Australia) and their controls on recharge, water level patterns and solutes of the superficial aquifer. Water Air Soil Pollut Focus 2005;5:3-26.

Sharma ML, Hughes MW. Groundwater recharge estimation using chloride, deuterium and oxygen-18 profiles in the deep coastal sands of Western Australia. J Hydrol 1985;81:93-109.

Sharma ML, Byrne JD, Herne DE, Kin PG. Impact of horticulture on water and nutrient fluxes to a sandy aquifer. CSIRO Division of Water Resources; 1991. Report 91/33, December.

Sommer B, Horwitz P. Macroinvertebrate cycles of decline and recovery in Swan Coastal Plain (Western Australia) wetlands affected by drought-induced acidification. Hydrobiologia 2009;624:191–203.

Stuiver M, Polach HA. Reporting of ^{14}C data. Radiocarbon 1977;19:355–63.

Tamers MA. Validity of radiocarbon dates on ground water. Geophys Surv 1975;2: 217–39.

Thorpe PM, Davidson WA. Groundwater age and hydrodynamics of the confined aquifers, Perth, Western Australia. Proceedings of the International Conference of Groundwater in Large Sedimentary Basins, Perth, Western Australia, 1990Australian Water Resources Council; 1991. p. 420–36. Conference Series no. 20.

Tipple BJ, Pagani M. The early origins of terrestrial C_4 photosynthesis. Annu Rev Earth Planet Sci 2007;35:435–61.

Tuffs A. Groundwater–surface water interaction along Gingin Brook Western Australia. Hydrogeology Record Series. Department of Water, Government of Western Australia; 2011 HG54.

Turner J, Yesertener C. The DOC-DIC transformation in acid buffering of WA coastal groundwaters. Abstract for 10th Australasian Environmental Isotope Conference & 3rd Australasian Hydrogeology Research Conference, Perth, WA; 2009.

Water Corporation. Integrated Water Supply Scheme–Water Resource Management Operation Strategy. Unpublished report for the Department of Water. Report 10/1088; 2010.

Wilson M, Garcia M. Sedimentology report on NG3 core, Gnangara Mound, Perth Basin, Department of Applied Geology, Curtin University, unpublished report for the Department of Water; 2009.

Yesertener C. Impacts of climate, land and water use on declining groundwater levels in the Gnangara Groundwater Mound, Perth WA. Aust J Water Resour 2005;8: 143–52.

Yu X. North Gnangara Mound drilling project proposal. Hydrogeology Report Series. Department of Water, Government of Western Australia; 2006 HR 242.

Zongyu C, Zhenlong N, Zhaoji Z, Jixiang Q, Yunju N. Isotopes and sustainability of ground water resources, North China Plain. Ground Water 2005;43:485–93.