A geochemical investigation of hydrologically derived threats to rare biota: the Drummond Nature Reserve, Western Australia

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Abstract The Drummond Nature Reserve (DNR), a high-value conservation area 100km northeast of Perth, Western Australia, contains two rare freshwater claypans and a diverse range of rare and threatened vascular plants. Groundwater/surface-water interactions were investigated via isotopic ($\delta^{18}O$ and δD) and major ion analysis. The groundwater chemical and isotope analyses combined with nutrient data allowed for the assessment of potential hydrologically derived threats to the claypans and their associated conservation values. Groundwater composition is typically Na–Cl to Na–Mg–Cl; whereas the claypan's ephemeral fresh surface water is Na–Cl–HCO_3. Distinct $\delta^{18}O$ and δD isotopic signatures for the claypan surface waters and adjoining groundwaters indicate that there currently is minimal connection between these two hydrological systems. Hence the current threat to the freshwater claypans and associated biota from rising saline and acidic groundwater is minimal. Elevated nutrient (N) levels identified in groundwaters along the reserve's western boundary may be linked to fertiliser regimes employed in adjoining agricultural lands. The ecosystem associated with the southwest claypan is particularly vulnerable to N and P inputs via surface-water flows, which could cause algal blooms, vegetation degradation and weed infestation.

Keywords Groundwater/surface-water relations · Freshwater claypans · Drummond Nature Reserve · Stable isotopes · Australia

Introduction

Groundwater discharge can be a major contributor to the water and salt balances of wetlands in arid and semi-arid regions (e.g., Williams 1999; Pinder et al. 2004; Jolly et al. 2008), primarily because rainfall is seasonal, highly variable and significantly less than the evaporation rate. As a consequence wetlands in such environments are prone to dry land or secondary salinization. These effects are mostly driven by human-induced changes to the hydrological cycle, which generate increasing recharge and rises in saline groundwater (Allison et al. 1990; Williams 1999). The wheatbelt region of Western Australia (Fig. 1) was extensively cleared of native vegetation during the 1900's for agricultural purposes, and is now greatly affected by secondary salinity (Clarke et al. 2002; George et al. 2008; Horwitz et al. 2008).

The Drummond Nature Reserve (DNR) located on the western margin of the Western Australian wheatbelt (Fig. 1), contains a diverse range (439 species) of vascular plants, several of which are rare and endangered (Keighery et al. 2002; Chow et al. 2010). Also located within the DNR are two freshwater claypans, which are the last such wetlands in the region that remain in their natural state (Kay 2001). These attributes resulted in the DNR being designated as a Natural Diversity Recovery Catchment under the Western Australian Government's State Salinity Strategy (Huston et al. 2000).

Several hydrological investigations have been undertaken in and around the DNR (Deshon 2000; Kay 2001; PPK 2002). These studies aimed to identify possible threats such as rising saline groundwaters and saline surface-water flows, to the condition of flora in the DNR's two freshwater claypans. However, none of these studies characterised the interactions between surface water and groundwaters, or the surface-water flows into the DNR. Nor did they define the threat from other aspects of altered hydrology such as excess nutrients. All of these processes must be sufficiently understood to assess the immediate and longer-term hydrological threats to the vegetation of the freshwater claypans and other flora throughout the DNR. This study aims to assess all possible hydrological derived threats to the DNR by characterising its surface-water and groundwater systems, primarily by the use of geochemical and isotopic analyses.

Alterations to water's chemical and isotopic composition occur when it interacts with the surrounding physical environment. Hence determining the chemical and isotopic composition of surface waters and groundwaters can provide insight into their origins, history and dynamics.

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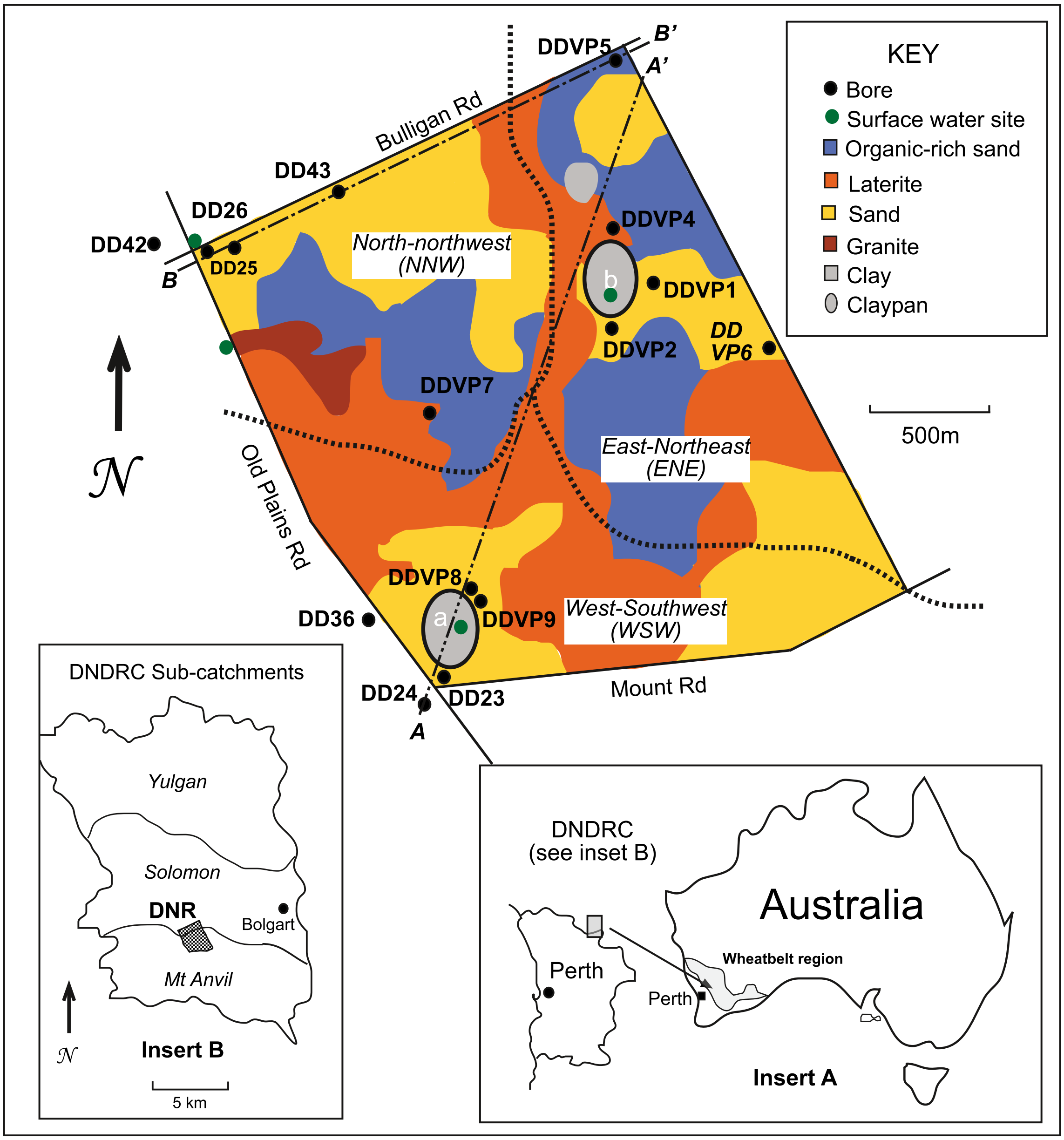

Fig. 1 Location of Drummond Nature Reserve (*DNR*), with respect to the *Yulgan*, *Solomon* and *Mt Anvil* sub-catchments and the Western Australian wheatbelt zone. Included are bore locations, separate sub-hydrological zones within the DNR (*dashed lines*) and transects (*A–A'* and *B–B'*) which are discussed later (see section Groundwater and surface-water dynamics). *DNDRC* refers to the Drummond Natural Diversity Recovery Catchment of which the Drummond Nature Reserve is a part

Numerous studies have applied stable oxygen and deuterium isotope techniques ($\delta^{18}O$ and δD) to investigate hydrological processes including, groundwater evolution and flow (e.g., Sharma and Hughes 1985; Arad and Evans 1987; Schofield and Jankowski 2004; Love et al. 2006; Bennetts et al. 2006), catchment dynamics and function (e.g., Herczeg et al. 1993; Cartwright et al. 2006; Hagedorn and Cartwright 2009), surface-water and groundwater interactions (e.g., Sharma and Hughes 1985; Cartwright et al. 2004; Marimuthu et al. 2005; Turner and Townley 2006) and lake mineral formation (e.g., Rosen et al. 1988, 1995; Wacey et al. 2007). Many of these groundwater isotope studies also used major-ion composition and ratios between ions to understand geochemical and hydrological processes.

Quantifying nutrient concentrations in surface waters and groundwaters, in particular nitrogen (N) and phosphorous (P), is important. Nutrient concentrations in surface waters and groundwaters are a critical issue in the southwest wheatbelt region of Western Australia, mainly because many of its sensitive ecological communities evolved under low soil and water nutrient levels (Prober and Smith 2009). Elevated concentrations of nutrients (in particular, nitrate, N_NO$_3^-$) are in many cases sourced from excess fertiliser applications in areas of intensive agriculture (Singh and Sekhon 1979; Correll et al. 1992; Shand and Edmunds 2008). Not only is the health of native biota vulnerable to such nutrient enrichment, but its presence is threatened

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by the competitive exclusion from exotic species, which increase in population levels as nutrient levels increase (Hobbs 1993; Prober and Smith 2009). This scenario is magnified in wetlands as they often have a greater capacity to accumulate solutes, including N and P (e.g., Devito and Dillon 1993), because they can act as landscape sumps.

This study aims to apply the previously discussed methods of geochemical analyses, combined with physical hydrological investigations, to understand the groundwater/surface-water interactions of the DNR. Particular focus is on the two claypans and their potential connection to the DNR groundwater system. Understanding the hydrological functioning will allow for the identification of current and an appreciation of possible future threats to the wetland ecosystems and the rest of the reserve from solutes, nutrients and acidity in groundwaters and surface waters.

Study area

The 439 ha DNR is located approximately 100 km northeast of Perth (Fig. 1). The reserve is part of the greater Drummond Natural Diversity Recovery Catchment (DNDRC) and prior to 1993, was freehold land that was intermittently logged for timber. The majority of the land surrounding the DNR has been cleared for agriculture, although some minor fringing areas have recently been re-vegetated.

Climate

The local climate is Mediterranean, with mild wet winters and hot dry summers. Most rainfall occurs between late autumn and early spring (April–September). Average annual rainfall (over last 100 years) recorded at the Bureau of Meteorology station (BoM 2010) at Bolgart 10 km northeast of the DNR is 460 mm. However, average yearly rainfall for the last two decades is lower (425 mm/year) than the 100 year average. Evaporation rates across the year on the whole are far greater than rainfall, although precipitation can exceed evaporation in winter months that experience above-average rainfall. Average (1975–2005) annual pan evaporation rates for the region are 1900 mm (BoM 2010), whereas average monthly rates for summer and winter are 300 and 100 mm respectively. Mean maximum and minimum temperatures for summer (January) are 34 and 17°C respectively, while for winter (July) the corresponding means are 17 and 5°C.

Geology and geomorphology

The DNR consists of a series of lateritic ridges underlain by highly weathered, Archaean (3.3–2.7 Ma) bedrock that is part of the Yilgarn Craton (Carter and Lipple 1982). The bedrock outcrops at numerous locations across the DNR and is intruded by numerous Proterozoic dolerite dikes (1–10 m thick), which trend north to northwest (Carter and Lipple 1982; Commander et al. 2001). The regolith is typical of many Western Australian landscapes (e.g., Anand and de Broekert 2005), it is composed of saprolite, overlain by a clayey pallid zone, which is in turn overlain by silcrete and laterite gravels (PPK 2002). The western, southern and central sections of the DNR are dominated by shallow bedrock (laterite and granite). The eastern and northern boundaries of the reserve are dominated by sands with similar substrates closely encircling both claypans. The two claypans themselves represent the lowest points in the DNR landscape and possess clay rich soils that are similar to those identified in other regional claypans (Featherstone and Brown 1990). These clay soils have accumulated in such environments via the reaction of magnesium rich waters with colloidal silica and minor amounts of alumina.

Hydrology and hydrogeology

The DNR straddles the boundary between the Solomon and Mt. Anvil sub-catchments (Fig. 1), with the northern third situated in the Solomon and the remainder in the Mt. Anvil. The central area of the DNR is characterised by a gentle undulating laterite plateau generating a topographic (bedrock) high that creates a surface water and groundwater divide between the reserve's northwest and southwest regions. This bedrock high represents the boundary in the DNR between the Solomon and Mt. Anvil sub-catchments. The claypans are situated in the southwest and northeast corners of the DNR. The southwest claypan is immediately adjacent (20 m) the reserve's southern and western boundaries. In comparison, the northeast claypan is located further within the reserves interior (500 m), and has distinct laterite and weathered granite bedrock highs proximal to its northern and western sides. Surface water flows from the west toward the southwest claypan and the northwest corner of the DNR (Kay 2001). These surface-water flows are characterised by several small fresh to brackish ephemeral tributaries located within the surrounding cleared farmland (Kay 2001). The DNR's two main aquifers are the weathered bedrock aquifer and the sand plain aquifer (Kay 2001; PPK 2002). The sand plain aquifer dominates the northern boundary and eastern half of the DNR and is comprised of mixed alluvial sand to sandy clay with occasional ferruginous zones. The weathered bedrock aquifer is a saprolite that is occasionally confined by overlying reworked saprolitic clays. This aquifer is much shallower in the interior of the reserve and along the southern and western boundaries, than it is in the remainder (PPK 2002). Surface waters in the two claypans are ephemeral, varying from dry in summer to a maximum winter depth of 50 cm (Huston et al. 2000). It has been theorised that these surface waters are possibly an expression of a rising groundwater table during the winter months (Kay 2001).

Biota

A plant survey undertaken by Keighery et al. (2002) identified at least 439 species of vascular plants, occurring within ten different vegetation types. These include the

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woodlands, *Eucalyptus wandoo* (Wandoo), *Banksia attenuate and B. menziesii* (Banksia)*, E. loxaphleba* (York gum) and *E. calophylla* (Marri), two granite heaths, a Mallee type, and the two claypan wetlands. The claypans are dominated by the shrub *Melaleuca lateritia*, and there are populations of the rare herbs *Hydatella leptogyne* and *Eleocharis keighery*, and plants *Hydrocotyle lemnoides* and *Schoenus natans*. The high density of these floras within the unique freshwater claypans is the primary reason for the conservation efforts at DNR (e.g., Chow et al. 2010). The Wandoo woodlands are generally associated with lateritic gravels, the Marri woodlands with organic-rich sandy silts, the Banksia woodlands with deep sands, and the *Melaleuca* with clays and occasional sands (Keighery et al. 2002). A survey of the claypans for aquatic invertebrates (Cale 2005) identified a very diverse community including three new species of *Rotifera* and two of *Ostracoda*. Many of the invertebrate species cannot tolerate major changes in water chemistry, in particular salt and nutrients.

Materials and methods

Field sampling

Ground and surface waters samples were collected at two designated seasonal intervals, the end of winter (September 2008) and the end of summer (May 2009). Rainfall for the sampling period was below the both the long-term and the last 20-year annual averages, with the Bolgart station recording 378 mm for 2008 and 414 mm for 2009 (BoM 2010). During the winter period, a total of 20 shallow (<10 m) and deep (>10 m) bores around the DNR were purged (3× bore volume removed) and sampled. In comparison only 11 of the deeper bore were sampled during the summer period, as many shallow bores were dry. A subsurface (1.6 m deep) bore established in the middle of each of the freshwater claypans was also sampled in winter. Automated high-resolution (hourly) monitoring of surface-water levels in both the claypans was undertaken with Schlumberger CTD-Divers, while bore water levels were measured manually on a monthly basis. Field measurements of water level, temperature, pH, electrical conductivity (EC) and oxidation-reduction potential (ORP) were taken at the time of sampling using the Hydrolab Quanta. ORP measurements (E_h) were corrected for the standard hydrogen electrode (SHE) relative to water temperature. Total alkalinity was also determined at the time of sampling using a Hanna HI3811 drop titration kit. Four surface-water sites were sampled during the winter period (Fig. 1): a small ephemeral stream flowing through a road culvert on the central western edge of the DNR ($\mathrm{CU_{SW}}$); an ephemeral pool located at the north western corner of the reserve (42_SW); and surface ($\mathrm{SW_{C1}}$; $\mathrm{NE_{C1}}$) and subsurface ($\mathrm{SW_{C2}}$; $\mathrm{NE_{C2}}$) waters in both claypans. Water samples for major ion and nutrient analysis were collected in HDPE bottles filled to overflowing and stored at <4°C until analysis. At each site a 50-ml sample was also collected, sealed in a small brown glass bottle and stored in darkness at <4°C for δ^{18}O and δD isotopic analysis.

Major ion and nutrient analysis

Samples were analysed at the Perth Chemistry Centre, Bentley, Western Australia for major ions ($\mathrm{Mg^{2+}}$, $\mathrm{Ca^{2+}}$, $\mathrm{Na^{+}}$, $\mathrm{K^{+}}$, $\mathrm{Cl^{-}}$, $\mathrm{Br^{-}}$, $\mathrm{F^{-}}$, $\mathrm{SO_4{}^{2-}}$) and nutrients (TN, $\mathrm{N\_NO_3{}^{-}}$, $\mathrm{N\_NH_3{}^{+}}$ and TP). Methods of analyses followed the procedures and guidelines outlined in APHA (1995). Calcium ($\mathrm{Ca^{2+}}$) and magnesium ($\mathrm{Mg^{2+}}$) were determined with volumetric titration using standard EDTA. Chloride ($\mathrm{Cl^{-}}$) was determined by standard $\mathrm{AgNO_3}$ titration. Fluoride ($\mathrm{F^{-}}$), nitrate ($\mathrm{N\_NO_3{}^{-}}$), bromide ($\mathrm{Br^{-}}$) and sulphate ($\mathrm{SO_4{}^{2-}}$) were estimated by spectrophotometer methods and sodium ($\mathrm{Na^{+}}$) and potassium ($\mathrm{K^{+}}$) were determined by flame photometry methods. Total nitrogen (TN) was determined using Kjeldahl digestion, total phosphorous (TP) was measured by ascorbic acid method and ammonia ($\mathrm{N\_NH_3{}^{+}}$) concentration was determined using the ammonia-selective electrode method. Analytical accuracy in the form of electrical neutrality (<5% deviation between anions and cations) is suggested via an electrical charge balance (Appelo and Postma 1993). $\mathrm{HCO_3{}^{-}}$ is an expression in mg/L of total alkalinity (ppm) determined in the field at the time of sampling.

Stable isotope analysis

Surface-water and groundwater samples were sent to the Commonwealth Science and Industrial Research Organisation (CSIRO), Land and Water, Adelaide, South Australia for δ^{18}O and δD analysis. The procedure used for oxygen isotope analysis is that described by Epstein and Mayeda (1953). CSIRO's modification to this procedure involved equilibration of $\mathrm{CO_2}$ with 1 ml in 6.5-ml exetainers in a temperature-controlled block held at 50°C for 8 h. The preparation and extraction of the $\mathrm{CO_2}$ was completed on a 59 port fully automated water-equilibrium system (WES) attached to a Europa Scientific Geo 20–20 dual inlet stable isotope mass-spectrometer. Quality control was maintained by placing the laboratory water standards—ROE and ROH deionised water calibrated to the international primary standards VSMOW (Vienna Standard Mean Ocean Water) and VSLAP (Vienna Standard Light Antarctic Precipitation)—at the beginning of each run, after every ten samples and at the end of the run. A similar equilibrium technique is used for deuterium analysis, this time hydrogen from the water molecules equilibrating with hydrogen gas. A platinum catalyst is used to enhance the exchange process, allowing complete exchange within 1 h. Stable isotope abundances are expressed as δ^{18}O and δD per mille (‰) relative to VSMOW. Duplicates were run every fifth sample for both δD and δ^{18}O, yielding an internal precision of ±0.15‰ for δ^{18}O and ±1.0‰ for δD.

Mineralogy

During the establishment of the shallow bores in the two claypans, 1.5 m of soil core samples were investigated at 10 cm intervals and documented. Subsequently, sediment samples for the northeast (30 and 100 cm depths) and southwest (40 and 130 cm depths) claypans were sent to CSIRO, Land and Water, Adelaide, South Australia for quantitative analysis by X-ray diffraction (XRD). Sample preparation followed procedures outlined by Moore and Reynolds (1989). Quantitative analysis was performed on the XRD data using the Rietveld method (Rietveld 1969) with the commercial package TOPAS from Bruker AXS. The results were normalized to 100%, and hence do not include estimates of unidentified or amorphous materials, and depending on the mineral, detection limits of 0.2% or less are achievable.

Results

Groundwater and surface-water dynamics

Based on geology and topography, the DNR can be delineated into three distinctive hydrological sub-regions (Fig. 1); namely the north northwest (NNW), east northeast (ENE) and west southwest (WSW). The northeast and southwest claypans are situated in the ENE and WSW sub-regions respectively. A peak of between 0.2 and 0.3 m in surface-water levels was identified in both claypans (Fig. 2) towards the end of the winter season (September 2008). Both claypans were dry by late spring (November), typical of this type of ephemeral wetland (e.g., Jolly et al. 2008; Prober and Smith 2009). EC is relatively fresh (1 mS/cm); however, a noticeable increase (up to 4 mS/cm) occurred during the spring months, reflecting a concentration of salts as the claypan surface water experienced seasonal evaporation.

Variable groundwater depths were observed across the DNR during the winter period. In several areas, in particular along the northern boundary of the reserve, groundwater levels were close to or at the ground surface. Groundwater levels in the WSW region were generally lower than those observed along the northern boundary; however, proximal to the southwest claypan depth to water was only 2–3 m. During the drier summer period groundwater levels generally dropped, with the majority of the shallow bores (<10 m) becoming dry. Seasonal fluctuations in groundwater levels were not as significant

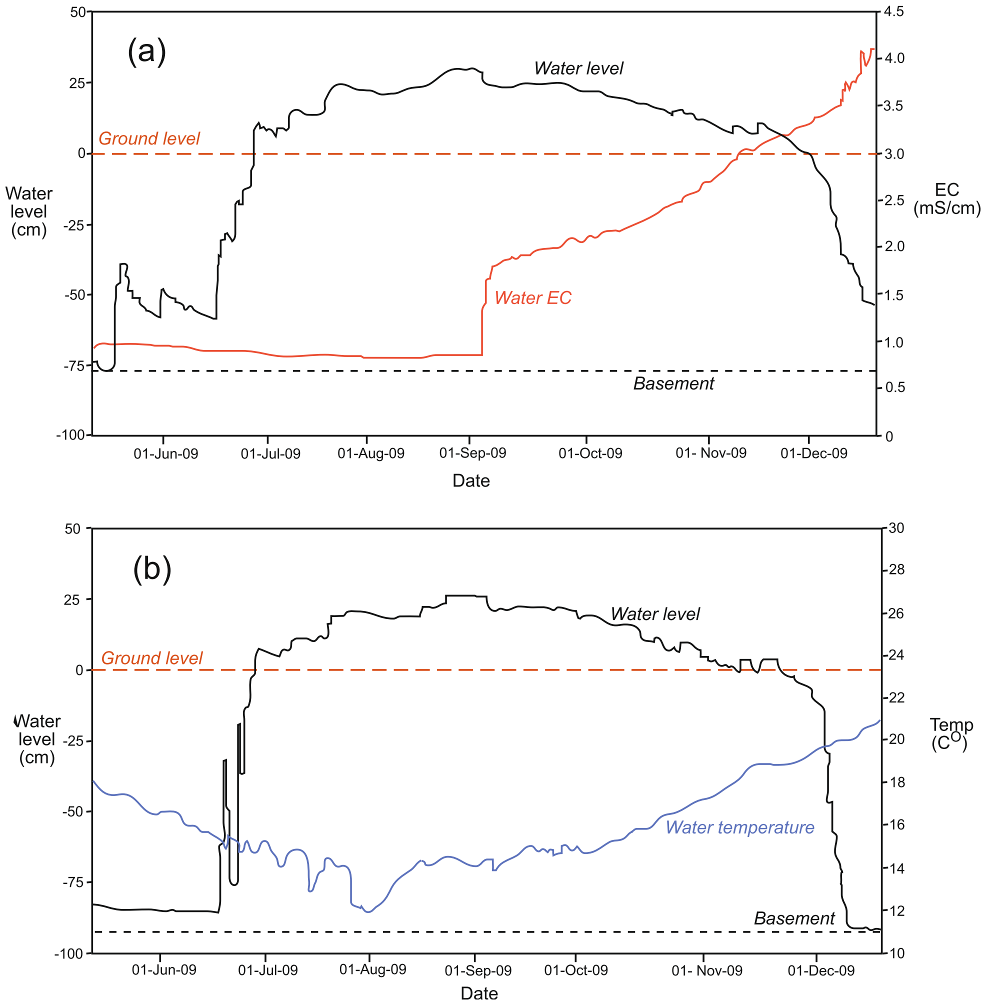

Fig. 2 Hourly water levels for both claypans for May to December 2009. The figure for the southwest claypan (**a**) shows water level and EC (mS/cm), while the figure for the northeast claypan (**b**) shows water level and temperature (°C). The marked increase in salinity observed in September 2009, which continues thereafter, is attributed to evaporation processes affecting the claypan surface and subsurface waters

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in the deeper bores (>10 m) with many remaining at a similar level or varying by around a metre.

Water levels in metres Australia Height Datum (mAHD) were plotted along two transects to examine groundwater depth and flow across the DNR. The first transect is from the southwest corner (A) to the northeast (A') corner, the second is west (B) to east (B') along the northern boundary of the DNR. Due to the variation in groundwater salinity and, hence, density throughout the DNR, water levels were first corrected to equivalent freshwater heads (Table 1) following methods outlined by Post et al. (2007). For transect A–A' (Fig. 3), surface elevation decreases from the southwest to the northeast with the depth to groundwater level generally following topography. Groundwater equipotentials and flow lines indicate that flow is from the west and southwest toward the reserve interior. Close to the southwest claypan marginally higher hydraulic heads in shallow groundwaters compared to deeper groundwater suggests some degree of downward movement of groundwater. Localised shallow groundwater inflow into the southwest claypan from the east is likely, via a perched groundwater system that is restricted to adjacent near-surface sandy sediments. The presence of substantial bedrock highs in the central DNR suggests that groundwater connectivity between the subregions containing the two claypans would be at best limited. The northeast claypan experiences localised groundwater flows from areas of shallow basement rock on its northern and western sides. Groundwater hydraulic heads around the northeast claypan suggest that the shallow groundwater behaves as a through flow system towards the east.

Surface elevation across transect B–B' (Fig. 4) is highest in the northwest (B), gradually decreasing towards the eastern boundary of the northeast claypan (B'). The water table follows surface topography, with groundwater flowing eastwards from the northwest corner. This flow regime is thought to terminate at the bedrock outcrop located adjacent to the western and northern boundaries of the northeast claypan. In this area groundwater hydraulic heads indicate a component of downward flow, and as such groundwater recharge.

A planar water-table contour map of the DNR was constructed based on observed groundwater levels, mapping of bedrock highs and a 0.5-m-scale digital elevation map (Fig. 5). In most parts groundwater flows from west to east; however, flow is altered in areas of shallow basement bedrock. Significant groundwater flow from the northwest concentrates in the central northern part of the DNR, due to the presence of bedrock highs south and east of this area. High water tables and substantial vegetation death are observed in this central northern area. It is also likely that groundwater continues from this area into the sand unit immediately to the north of the DNR. Groundwater flows from the west and southwest towards the southwest claypan, which based on local hydraulic head values, then appears to be recharging downwards below the claypan. There also seems to be localised easterly flow of shallow subsurface waters into the claypan. The extent of this flow is questionable as the shallow bores on the eastern side of the claypan are not very responsive and dry out over the summer months. The presence of a northeast trending basement rock high suggests hydrological separation of the two claypans. Groundwater flows from the eastern side of the basement rock high through the northeast claypan area east and south towards the deep sand deposits along the eastern margin of the DNR.

Claypan stratigraphy and mineralogy

The top 1.5 m of sediments in both claypans is characterised by three general sedimentary layers. An organic matter bearing (3–5%) topsoil (20 cm thick) followed by an underlying (40 cm thick) silty clay layer, mixed with moderately angular quartz grains. Below this are thick (>40 cm) olive/green clays. Quantitative mineralogical analysis (XRD) of sediments at 40 and 100 cm depth intervals indicates that the clays kaolinite (45–48%) and glauconite-illiite (42–50%) are the dominant mineral constituents, followed by lesser amounts of quartz (<10%), halite, calcite, and feldspar (2%).

EC, pH and ORP

Winter groundwaters were acidic to slightly acidic (pH 5.0–6.5), becoming more acidic (pH 4.6–6.3) during summer (Table 1). This pH range is common among groundwaters of the Western Australian wheatbelt (e.g., Degens et al. 2008). Less acidic pH values (6–7) were observed for surface waters. EC levels were variable, ranging from marginal (100 mS/m) to brackish (600 mS/m) for groundwaters. Winter samples were generally fresher than their summer equivalents with EC values falling by as much as half. Winter claypan surface-water EC values were fresh (20–60 mS/m) as were several adjacent shallow bores. In comparison, surface waters located in the northwest corner of the reserve were brackish (842 mS/m). Furthermore much greater EC levels (3,000–4,000 mS/m) compared to the majority of groundwaters were observed for shallow groundwater in the northwest corner ($D26_{OB}$).

Oxidation-reduction potentials (ORP) of both ground and surface waters ranged between 200 and 500 mV, indicating predominantly oxidising conditions (Table 1). Oxidising conditions still prevailed for groundwater in the summer, despite a decrease in ORP (16–288 mV) being observed. In fact ORP values at two sites (D8 and D23D), both adjacent the southwest claypan became negative in the summer (approx. −150 mV), implying a shift from oxidising to reducing conditions in these groundwaters.

Major ion chemistry

All DNR groundwaters (Table 1; Fig. 6) are dominated by Na^+ and Cl^- (mostly >90%); with Cl^- strongly correlated (R^2=0.92) with EC (salinity). Relative abundances between ions is similar for both summer and winter; however, total ion content is greater for most summer groundwaters (in some cases significantly). Saline shallow

Table 1 Ionic composition, salinity, alkalinity, redox potential, pH, nutrient levels and isotopic composition of surface and groundwater samples from Drummond Nature Reserve for samples collected at the end of winter (September 2008) and summer (May 2009)

Site	Water level[a] (mA SL)	pH	ORP (mV)	EC (mS/m)	Ca^{2+} (mg/L)	Cl^{-} (g/L)	Na^{+} (g/L)	Mg^{2+} (mg/L)	K^{+} (mg/L)	HCO$_3^{-b}$ (mg/L)	SO$_4^{2-}$ (mg/L)	Br^{-} (mg/L)	N_NO$_3^{-}$ (mg/L)	N_NH$_3^{+}$ (mg/L)	TN (mg/L)	TP (mg/L)	δ^{18}O ‰	δ^{2}H ‰
Winter 2008: surface waters																		
SW$_{C1}$	0.0	6.2	293	18	1	0.04	0.02	1	19	61	1	0.02	0.01	0.14	1.4	0.0	–2.4	–4.7
NE$_{C1}$	0.0	6.7	218	22	1	0.04	0.03	1	6	24	2	0.02	0.01	0.08	1.4	0.0	–1.8	–1.5
SW$_{C2}$	0.0	6.3	182	17	2	0.05	0.03	4	19	24	31	0.02	0.01	0.02	17.0	0.3	–2.3	–6.4
NE$_{C2}$	0.0	6.9	216	21	1	0.05	0.03	1	7	25	2	0.02	0.10	0.09	2.0	0.1	–1.9	–1.1
42$_{SW}$	0.0	6.1	171	72	20	0.44	0.16	37	4	23	4	1.3	0.01	0.09	1.5	0.1	–3.7	–14.6
CU$_{SW}$	0.0	6.2	12	842	78	4.83	1.77	419	4	27	294	11	0.01	0.08	0.2	0.0	–4.0	–16.1
Winter 2008: groundwaters																		
D2	274.7	5.6	229	72	3	0.33	0.15	10	16	29	132	0.36	0.00	0.02	12.0	0.5	–5.0	–18.1
D5	272.8	5.9	215	192	22	1.12	0.51	91	3	58	91	1.2	0.00	0.02	0.3	0.1	–5.1	–21.7
D6	276.5	5.6	195	25	1	0.06	0.05	2	2	13	25	0.2	0.20	0.39	3.0	0.1	–5.2	–22.3
D7$_{D}$	281.1	5.0	174	604	7	1.93	1.09	132	5	2	167	3.1	0.01	0.05	0.5	0.1	–5.2	–22.7
D8	283.0	6.4	44	156	7	0.41	0.26	13	8	103	32	1.1	0.01	0.08	0.9	0.0	–4.9	–23.4
D9	280.8	5.6	210	21	1	0.12	0.07	3	2	5	12	0.12	0.09	0.03	0.9	0.0	–4.3	–19.5
D23$_{OB}$	284.8	6.4	72	632	23	4.22	1.68	411	2	35	53	10	0.04	0.19	2.0	0.1	–4.7	–23.9
D23$_{D}$	282.8	5.5	35	630	12	4.71	2.61	326	3	85	459	11	0.00	0.66	0.7	0.0	–5.0	–21.8
D23$_{D1}$	283.0	5.0	190	138	3	4.20	0.58	68	7	3	109	0.5	1.50	0.00	2.5	0.0	–4.8	–23.4
D24$_{D}$	283.6	4.9	265	481	10	2.83	1.62	208	31	15	238	7.7	0.62	0.04	1.1	0.0	–4.7	–21.0
D25$_{D}$	294.6	5.2	197	567	35	3.92	1.59	225	16	42	449	8.7	0.00	0.02	0.1	0.0	–4.6	–20.1
D26$_{OB}$	293.4	6.0	24	3,010	278	11.5	5.35	1,170	10	35	608	31	0.00	0.00	0.4	0.0	–3.9	–16.2
D36$_{OB}$	282.1	5.1	300	130	1	0.49	0.34	19	12	5	112	1.2	3.40	0.00	4.6	0.0	–4.6	–21.2
D42$_{D}$	300.5	5.6	159	624	41	3.21	1.79	261	22	32	320	8.3	0.00	0.02	0.1	0.3	–4.8	–23.1
D42$_{OB}$	300.2	6.2	27	535	3	2.17	1.38	113	3	26	253	5.6	0.0	0.04	1.7	0.1	–4.9	–22.2
D43$_{OB}$	281.2	5.9	95	25	4	0.04	0.03	7	1	10	11	0.09	3.10	0.00	3.1	0.0	–5.4	–26.2
D43$_{D}$	280.8	5.3	170	60	1	0.15	0.09	8	3	6	17	0.42	2.50	0.00	3.1	0.0	–4.8	–22.8
Summer) 2009: groundwaters																		
D5	272.4	5.5	16	375	22.4	1.12	0.61	90	3	99	75	4	0.09	0	0.5	0.1	–4.7	–23.3
D7$_{D}$	281.0	4.6	218	605	7.1	1.78	1.07	134	4	37	156	6.7	0.01	0.02	1.3	0	–4.9	–23.4
D8	280.8	6.3	–145	197	5	0.51	0.38	15	10	183	30	1.7	0.01	0.17	1.2	0.2	–4.7	–23.3
D23$_{D}$	282.1	5.2	–188	1,480	14.4	4.80	2.70	352	3	137	427	14	0	0.24	1.0	0	–4.7	–23.5
D23$_{D1}$	282.8	4.9	217	372	4	1.12	0.62	75	7	37	124	2	2.7	0	5.9	0	–4.7	–21.7
D24$_{D}$	282.3	4.8	288	828	7.2	2.60	1.38	180	26	53	234	7.4	2.1	0	3.2	0	–4.4	–21.5
D25$_{D}$	294.1	5.2	179	1,110	46.8	3.57	1.89	287	19	88	393	10	0	0.03	0.2	0	–4.4	–21.5
D26$_{OB}$	291.1	5.7	87	4,340	245	19.90	8.67	1,880	9	137	1,350	51	0	0	1.0	0	–4.0	–21.7
D36$_{OB}$	281.7	4.9	192	194	1.6	0.51	0.36	19	13	40	116	1.4	5.9	0	9.4	0.1	–4.1	–20.3
D42$_{D}$	297.2	5.4	149	985	39.6	2.99	1.69	251	20	77	309	6.4	0	0	0.2	0.1	–4.5	–22.7
D43$_{D}$	279.7	5.2	196	70	1.7	0.15	0.11	10	3	40	19	0.5	6.2	0	9.9	0	–4.3	–21.9

[a] Water Levels presented here have been converted to fresh water equivalents compensating for density variations

[b] HCO$_3^{-}$ values are a mg/L expression of total field alkalinity

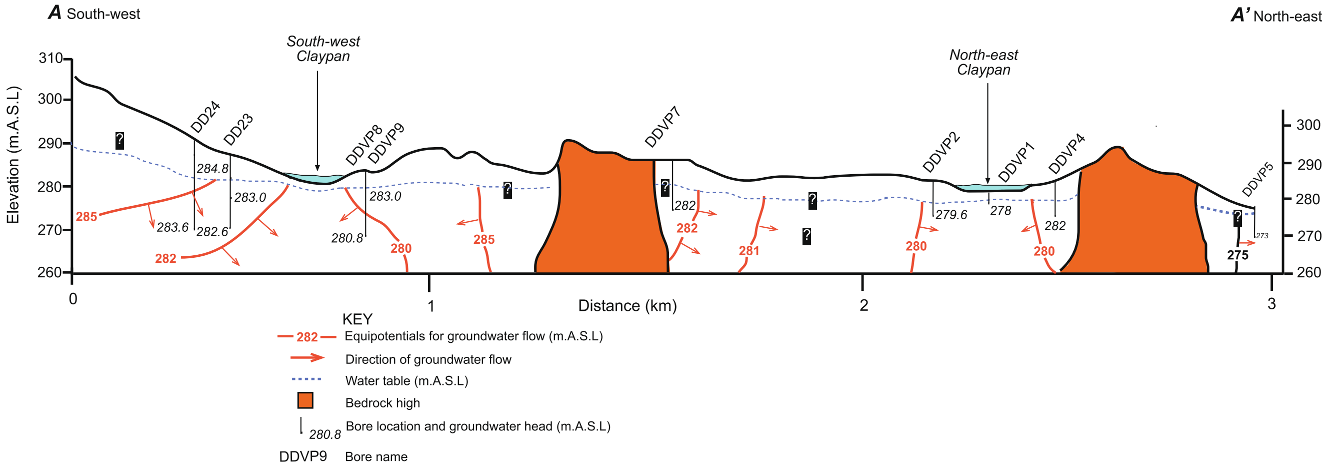

Fig. 3 Groundwater flow cross section for a southwest (*A*) to northeast (*A'*) transect across the DNR, incorporating both the southwest and northeast claypans

groundwater ($D26_{OB}$) in the northwest corner of the reserve has Cl^- and Na^+ concentrations of 20,000 and 8,600 mg/L (respectively) in summer, whereas elsewhere concentrations are generally below 5,000 (Cl^-) and 2,500 (Na^+) mg/L. SO_4^{2-} concentrations up to 5% total ion content are observed, particularly in the western part of the reserve. Concentrations of HCO_3^- are typically lower than SO_4^{2-}, and are highest around the southwest claypan. Mg^{2+} is more prominent than either Ca^{2+} or K^+. Br^- is observed in relative minor concentrations compared to other major ions. Concentrations of F^- are generally below detection limits (< 0.05 mg/L) and will be no longer discussed.

The claypan surface and sub-surface waters are dominated by Na^+ and Cl^-, but have a greater representation by HCO_3^- compared to the groundwaters (Fig. 6). Unlike the groundwaters there is little correlation between EC and Cl^- (R^2=0.244) in claypan surface waters. Total ion content is significantly lower in the claypan surface waters than in the groundwaters. SO_4^{2-} concentrations are minor (<30 mg/L), whereas K^+ concentrations (up to 20 mg/L) are greater than Mg^{2+} and Ca^{2+}, and Br^- (0.02 mg/L) is minor. The saline surface water in the northwest corner of the DNR has an ionic composition more akin to the groundwaters, rather than the claypan surface waters (Fig. 6).

Nitrogen and phosphorous

Total nitrogen (TN) content (Table 1) for surface waters and groundwaters are generally low (0.1–5 mg/L). However, higher values are observed in groundwater proximal to the northeast (12 mg/L at D2) claypan, and for the southwest claypan sub-surface water (17 mg/L at SW_{C2}). These two higher TN values coincide with low nitrate ($N\_NO_3^-$) and ammonia ($N\_NH_3^+$) concentrations. Groundwater along the reserve's western boundary ($D43_{OB}$, $D43_D$, $D23_{D1}$, and $D36_{OB}$) displays higher TN values, in particular during the summer period (5–10 mg/L). These higher TN concentrations are dominated by inorganic forms of N (nitrate and ammonia) and exceed the 4 mg/L threshold proposed by Prober and Smith (2009) required for the protection of native vegetation in the Western Australian wheatbelt. Total phosphorous (TP) concentrations are low across the entire DNR (≤0.5 mg/L), do not fluctuate seasonally, and fall well below the Prober and Smith (2009) native vegetation threshold (5 mg/L).

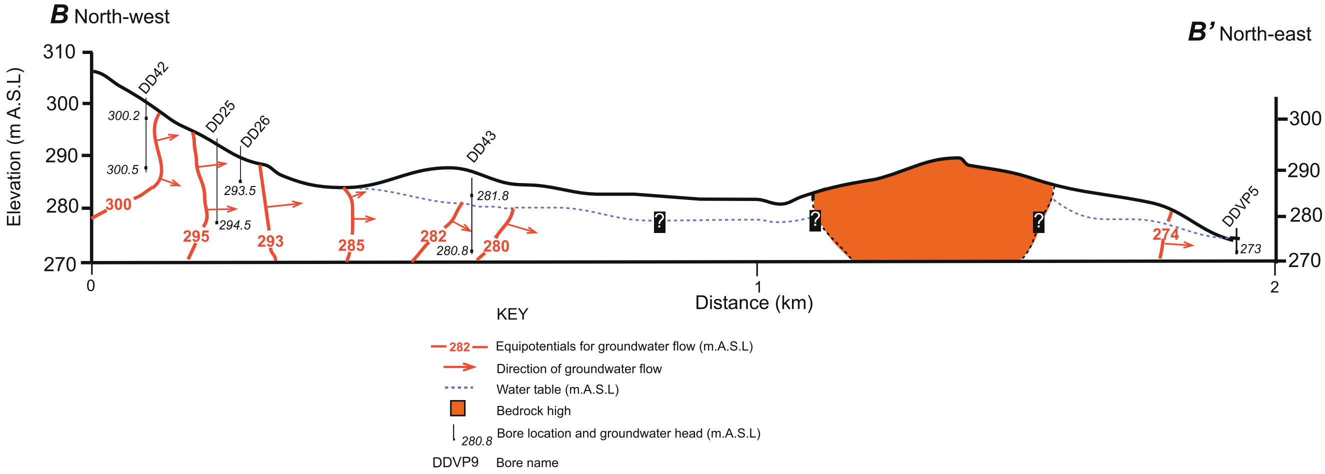

Fig. 4 Groundwater flow cross section for a northwest (*B*) to north (*B'*) transect along the DNR's northern boundary

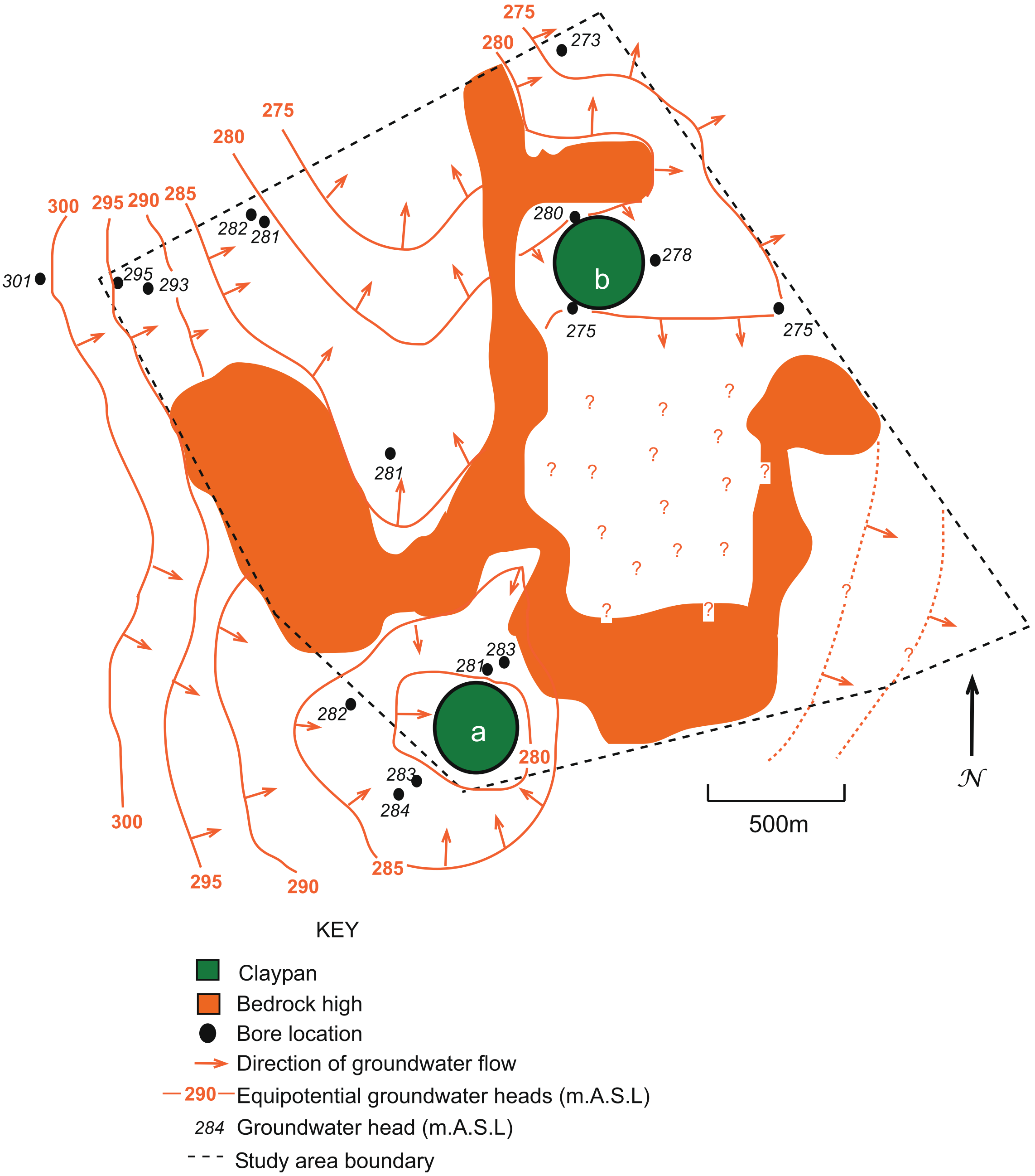

Fig. 5 Plan view of groundwater flow across the DNR. This flow is predominantly west to east; however, it is modified in some areas by the presence of local bedrock highs

Oxygen and hydrogen stable isotopes

Comparisons of stable oxygen ($\delta^{18}O$) and deuterium (δD) isotopic data for the claypan surface and subsurface waters and the groundwaters see markedly different signatures between the two (Table 1). Isotopic signatures for claypan surface and subsurface waters are −2.4 and −1.8‰ for $\delta^{18}O$ and −6 and −1‰ for δD. Winter groundwaters range between −5.4 to −3.9‰ ($\delta^{18}O$) and −26 to −18‰ (δD), whereas summer groundwater isotopic signatures are −4.9 to −3.9‰ ($\delta^{18}O$) and −23 to −20‰ (δD). The surface waters located in the NNW sub-region display less-enriched $\delta^{18}O$ (−4.0 to −3.7‰) and δD (−16 to −14‰) isotopic signatures than the claypan waters. Rather these two surface-water samples display isotopic signatures that are very similar to shallow groundwater proximal to their location ($D26_{OB}$; $\delta^{18}O$ −3.8‰, δD −16‰).

Discussion

Hydrological interpretations

Results presented and discussed in this study have broadened substantially the understanding of the hydrological dynamics of the DNR. Interpretations of hydrodynamic data indicate that the predominant groundwater flow is west to east across the reserve. A zone of

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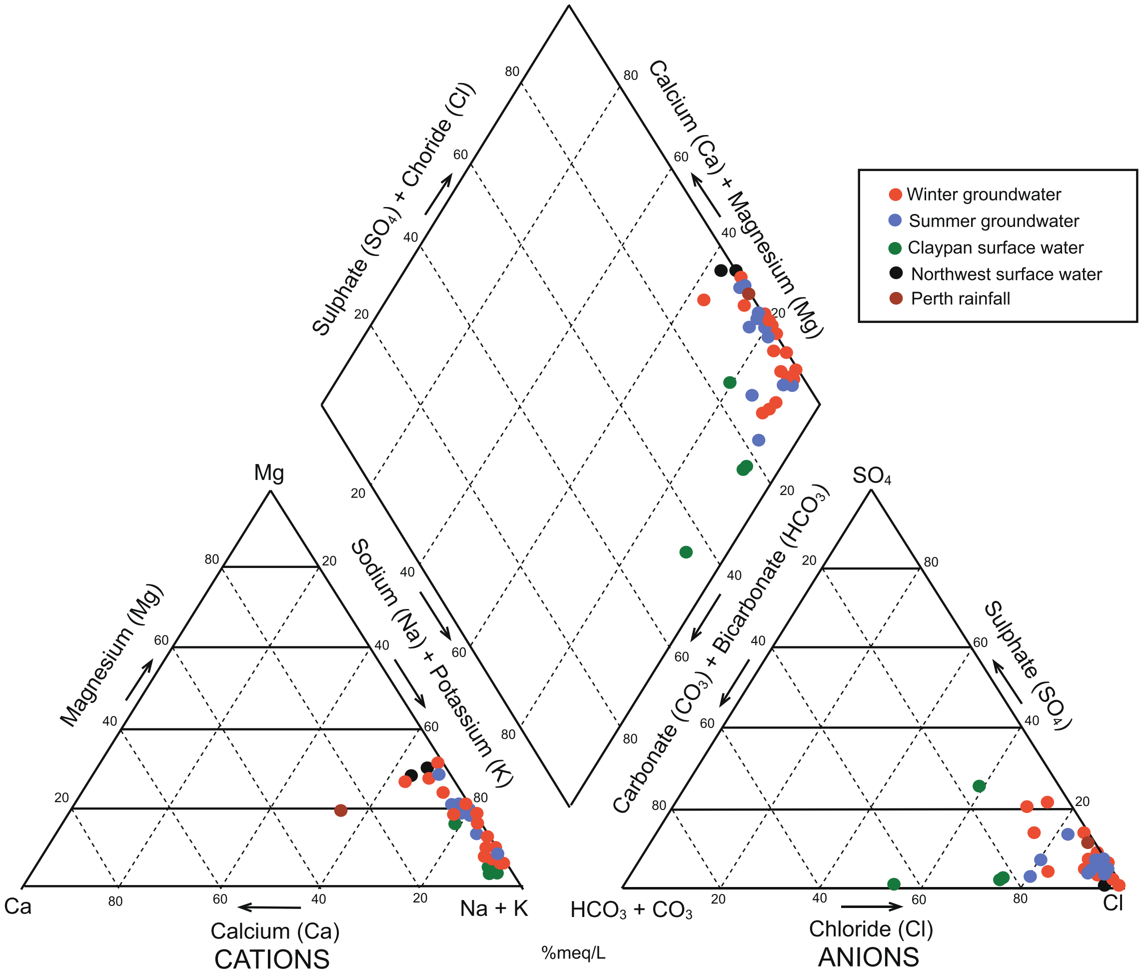

Fig. 6 Piper diagram for surface waters, *summer groundwaters* (May 2009) and *winter groundwaters* (September 2008) for the Drummond Nature Reserve. Rainfall data are taken from Hingston and Gailitis (1976)

groundwater convergence is identified in the central-northern part of the DNR, resulting from bedrock highs situated to the south and east (roughly corresponding with the Solomon-Mt. Anvil sub-catchment divide). This geomorphology also explains the presence of shallow water tables, groundwater seeps and vegetation death in that area. Groundwater is theorised to then flow from the area of convergence into the porous sandy substrates located directly to the north of the DNR. On the eastern side of the bedrock high groundwater flow is both east and southward through the northeast claypan, also into porous sandy substrates, that define the eastern section of the reserve.

In the southern part of the DNR, groundwater flows from the west and southwest, towards the southwest claypan. The presence of bedrock highs to the east and north of the southwest claypan and the current hydraulic head gradient means groundwater flow is likely to be recharging downwards below the southwest claypan. This centrally located bedrock high combined with anticipated small hydraulic gradients (thus slow flow), suggests that groundwater connectivity between the two claypan regions is most unlikely. Easterly flows of shallow subsurface water also appear to be feeding into the southwest claypan. However, these flows are minimal, occurring only after significant rainfall recharge events, and thus act solely as a transport mechanism for fresh seasonal rainfall into the southwest claypan. It would appear that the connection between the deeper weathered bedrock aquifer and the shallower sand aquifer are limited here and elsewhere throughout the southern half of the DNR. Historical water levels for the three bores (Fig. 7) close to the southwest claypan indicate that groundwater fluctuations in the weathered bedrock aquifer ($DD23_{D1}$ and $DD23_{D}$) are different to that in the shallow sand aquifer ($DD23_{OB}$) and promote minimal connection between the two. Significant seasonal fluctuations, including becoming dry in summer months, are observed in the sand aquifer, whereas smaller fluctuations, which appears much less responsive to seasonal dynamics, are evident for the weathered bedrock aquifer. This current lack of significant hydrological connectivity between the weathered bedrock aquifer and shallow sand aquifer, and in turn the claypan may change if deeper groundwater levels around the southwest claypan were to rise.

Hydrochemistry

The Na^+ and Cl^- dominant groundwaters on the DNR is typical of many Australian groundwaters (Arad and Evans

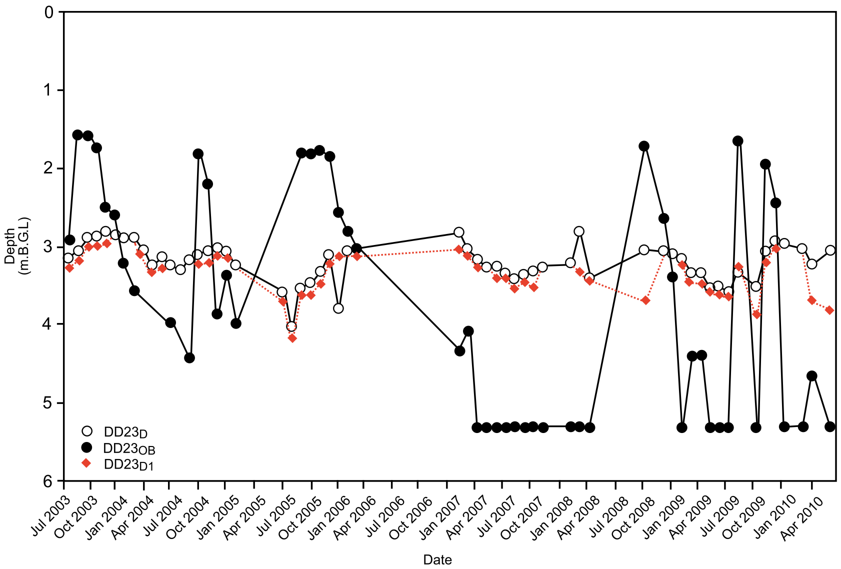

Fig. 7 Historical monthly water levels for the three nested bores located on the southern edge of the southwest claypan. These data are manual bore dip measurements. The baseline minimum in $DD23_{OB}$ is in fact the bottom of the bore and represents a dry reading. Depth fluctuations in the shallow bore ($D23_{OB}$) representing the sand aquifer are dramatic and appear strongly seasonal. In comparison depth fluctuations in deeper bores ($DD23_{D}$ and $DD23_{D1}$) associated with the weathered bedrock aquifer is less so, suggesting minimal connection between the two

1987; Herczeg et al. 1991; Salama et al. 1993), and especially so for the Western Australian wheatbelt (Hingston and Gailitis 1976; Clarke et al. 2002). In contrast to the groundwater, Na^+ and Cl^- contents in the claypan surface waters are lower, with a greater HCO_3^- representation. This HCO_3^- could originate from the dissolution of CO_2 during mineral weathering, organic matter breakdown or via local subsurface runoff containing carbonates (Appelo and Postma 1993). Considering the presence of clay minerals, organic matter and calcareous sands that fringe the claypan, all three could be contributing to the HCO_3^- content.

In order to understand the processes that shaped the chemistry of the surface waters and groundwaters within the DNR, molar ratios of major ions (Na+, K+, Mg^{2+}, Ca^{2+}, HCO_3^- and SO_4^{2-}) against Cl^- (Table 2) were compared to similar ratios of regional rainfall (Hingston and Gailitis 1976). These ionic ratios are calculated against Cl^- as it is considered to be relatively inert (e.g., Feth 1981). For the southwest claypan losses of both Ca^{2+} and Mg^{2+} relative to regional rainfall were identified, along with a smaller loss of Na^+ and a minor gain of K^+. Similar trends were identified for the subsurface water in the southwest claypan, except for a slight loss of K^+. In comparison, the northeast claypan saw general gains of K^+ and Na^+ relative to rainfall and losses of Mg^{2+} and Ca^{2+}, but K^+ was lost from the sub-surface water rather than gained. The losses of Mg^{2+} and Ca^{2+} are likely reflecting ion exchange where high-valence cations out compete the univalent cations (Na^+ and K^+) for sorption sites on the clay matrix. The K^+ gains in the surface waters of both claypans (more so in the northeast claypan) can be attributed to not only ion exchange, but also the significant presence of illiite in the sediments. Illite has been identified as a significant source of K^+ elsewhere in Australia (McArthur et al. 1989; Salama et al. 1993), concentrating in the clay sediments and becoming soluble during the wet winter months.

For both summer and winter groundwaters significant decreases in Ca^{2+}, K^+ and Mg^{2+} relative to rainfall were observed for the vast majority. In comparison Na^+ changes, while variable mostly increased relative to rainfall. As with the surface water, increases of Na^+ and decreases of Ca^{2+} and Mg^{2+} (and in this case K^+ as well), are attributed to ionic exchange between groundwaters and the aquifer matrix. Both SO_4^{2-} and HCO_3^- in groundwater exhibit general losses relative to regional rainwater, but some slight increases in the claypan surface waters. Investigations of Ca^{2+} and SO_4^{2-} molar concentrations, expressed as $Ca^{2+}/(Ca^{2+} + SO_4^{2-})$, against pH (Fig. 8) have been used previously by Hounslow (1995) to distinguish between processes that effect the ionic composition of groundwater. Evident is that many processes are possibly contributing to the groundwater chemistry of the DNR, including calcite precipitation, gypsum dissolution and pyrite oxidation all contributing to groundwater chemistry. These data are a possible reflection of aquifer heterogeneity across the DNR and also likely groundwater mixing over time. Also apparent from the data is that chemical composition of the claypan surface waters can be in part attributed to carbonates.

Greater Cl^- (42–52 mg/L) and Na + (19–34 mg/L) concentrations for the fresh claypan surface waters in comparison to regional rainfall (2–6 mg/L and 1–3 mg/L respectively; Hingston and Gailitis 1976) suggests concentration of these ions during the spring time evaporation. However, Cl/Br ratios for the claypan surface waters indicate that rainfall is possibly not the only source of Cl^-. While Cl^- and Br^- are ubiquitous solutes in natural groundwater systems and generally originate from atmos-

Table 2 Molar ratios for surface water and groundwaters for Drummond Nature Reserve

	Na/Cl	Ca/Cl	K/Cl	Mg/Cl	SO$_4$/Cl	HCO$_3$/Cl
Seawater[a]	0.859	0.019	0.019	0.097	0.052	0.004
SW central rain[a]	0.802	0.146	0.354	0.059	0.148	0.639
Winter 2008: surface water						
$\mathrm{SW}_{\mathrm{C1}}$	0.7052	0.0211	0.4145	0.0000	0.0062	0.8395
$\mathrm{NE}_{\mathrm{C1}}$	1.1675	0.0281	0.1319	0.0000	0.0151	0.3141
$\mathrm{SW}_{\mathrm{C2}}$	0.7328	0.0255	0.3295	0.0002	0.2193	0.2626
$\mathrm{NE}_{\mathrm{C2}}$	1.1192	0.0188	0.1331	0.0000	0.0141	0.3148
42_{SW}	0.5575	0.0396	0.0091	0.0015	0.0034	0.0306
$\mathrm{CU}_{\mathrm{SW}}$	0.5653	0.0143	0.0008	0.0172	0.0225	0.0032
Winter 2008: groundwater						
D2	0.7199	0.0088	0.0451	0.0038	0.1476	0.0515
D5	0.7052	0.0176	0.0024	0.0001	0.0300	0.0302
D6	1.0896	0.0126	0.0288	0.0054	0.1447	0.1238
$\mathrm{D7}_{\mathrm{D}}$	0.8712	0.0033	0.0023	0.0005	0.0319	0.0007
D8	0.9646	0.0155	0.0181	0.0001	0.0286	0.1458
D9	0.8755	0.0098	0.0186	0.0169	0.0372	0.0247
$\mathrm{D23}_{\mathrm{OB}}$	0.6141	0.0048	0.0003	0.0134	0.0046	0.0048
$\mathrm{D23}_{\mathrm{D}}$	0.8548	0.0023	0.0005	0.0028	0.0360	0.0104
$\mathrm{D23}_{\mathrm{D1}}$	0.7469	0.0024	0.0054	0.0086	0.0335	0.0015
$\mathrm{D24}_{\mathrm{D}}$	0.8831	0.0031	0.0100	0.0093	0.0310	0.0030
$\mathrm{D25}_{\mathrm{D}}$	0.6257	0.0079	0.0037	0.0481	0.0423	0.0063
$\mathrm{D26}_{\mathrm{OB}}$	0.7177	0.0214	0.0008	0.0008	0.0195	0.0018
$\mathrm{D36}_{\mathrm{OB}}$	1.0726	0.0025	0.0226	0.0107	0.0845	0.0058
$\mathrm{D42}_{\mathrm{D}}$	0.8602	0.0113	0.0062	0.0046	0.0368	0.0057
$\mathrm{D42}_{\mathrm{OB}}$	0.9810	0.0012	0.0011	0.0003	0.0430	0.0069
$\mathrm{D43}_{\mathrm{OB}}$	1.0835	0.0821	0.0130	0.0003	0.0949	0.1333
$\mathrm{D43}_{\mathrm{D}}$	0.9043	0.0079	0.0181	0.0000	0.0428	0.0248
Summer 2009: groundwater						
D5	0.8388	0.0177	0.0021	0.0037	0.0246	0.0513
$\mathrm{D7}_{\mathrm{D}}$	0.9273	0.0035	0.0021	0.0055	0.0323	0.0119
D8	1.1329	0.0086	0.0179	0.0006	0.0218	0.2076
$\mathrm{D23}_{\mathrm{D}}$	0.8677	0.0027	0.0006	0.0145	0.0328	0.0166
$\mathrm{D23}_{\mathrm{D1}}$	0.8485	0.0032	0.0058	0.0031	0.0409	0.0190
$\mathrm{D24}_{\mathrm{D}}$	0.8188	0.0024	0.0090	0.0074	0.0332	0.0119
$\mathrm{D25}_{\mathrm{D}}$	0.8167	0.0116	0.0047	0.0118	0.0406	0.0143
$\mathrm{D26}_{\mathrm{OB}}$	0.6721	0.0109	0.0004	0.0774	0.0250	0.0040
$\mathrm{D36}_{\mathrm{OB}}$	1.1067	0.0028	0.0229	0.0008	0.0846	0.0462
$\mathrm{D42}_{\mathrm{D}}$	0.8719	0.0117	0.0062	0.0103	0.0381	0.0149
$\mathrm{D43}_{\mathrm{D}}$	1.1621	0.0100	0.0199	0.0004	0.0470	0.1559

[a] Molar ratios for seawater and regional rainfall were calculated from data by Hingston and Gailitis 1976

pheric fallout (wet and dry); Cl$^-$ can also come from the dissolution of evaporates, while it's not a major source of Br$^-$ (e.g., Ullman 1995; Davis et al. 1998, 2001; Herczeg and Edmunds 2000; Cartwright et al. 2006). Hence water originating from such evaporates exhibit higher Cl/Br ratios to those dominated by atmospheric deposition. Cl/Br weight ratios of 297 have been identified for seawater and coastal rainfall (Davis et al. 1998). In contrast dissolution of sedimentary halite results in Cl/Br weight ratios of over 1,000; reflecting increasing contributions by Cl$^-$ relative to Br$^-$ (Cartwright et al. 2004). Cl/Br weight ratios (Fig. 9) for the DNR's claypan surface and subsurface waters are an order of magnitude greater (>2,000) than they are for groundwater (300–600), which are close to seawater ratios. The increase in Cl$^-$ concentrations and subsequent high Cl/Br ratios in the claypan surface and sub-surface waters could be attributed to in-situ dissolution of minor amounts of halite, which has been identified in the claypan sediments. However, low (0.02 mg/L) Br$^-$ concentrations within the claypans are just above detection limits (0.01 mg/L), as such even minor increase in Cl$^-$ would increase Cl/Br ratios markedly. Hence, while the distinct separation of Cl/Br weight ratios between the groundwaters and claypan surface waters suggests a lack of hydrological conductivity between the two, such interpretations of this data should be made in conjunction with other geochemical data presented in this study.

Stable oxygen and deuterium isotopes

Distinctly different δ^{18}O and δD signatures are observed for the majority of groundwaters, compared to the claypan surface waters, with the latter being more enriched in δ^{18}O and δD (Fig. 10). This isotopic separation suggests a lack of hydrological connectivity between the claypan surface water and the deeper groundwater system. It is most likely that the composition and depth (>3 m) of the claypan sediments have created a semi-impermeable barrier that has resulted in only minor downward leakage of surface waters. Thus the resulting lack of connectivity between the two means most surface water is evaporated from the claypans, rather than recharged at slow time scales.

Insufficient δ^{18}O and δD data for local rainfall was available to generate a local meteoric water line (LMWL), hence a MWL for Perth (δD=7.15 × δ^{18}O+10.6; Turner

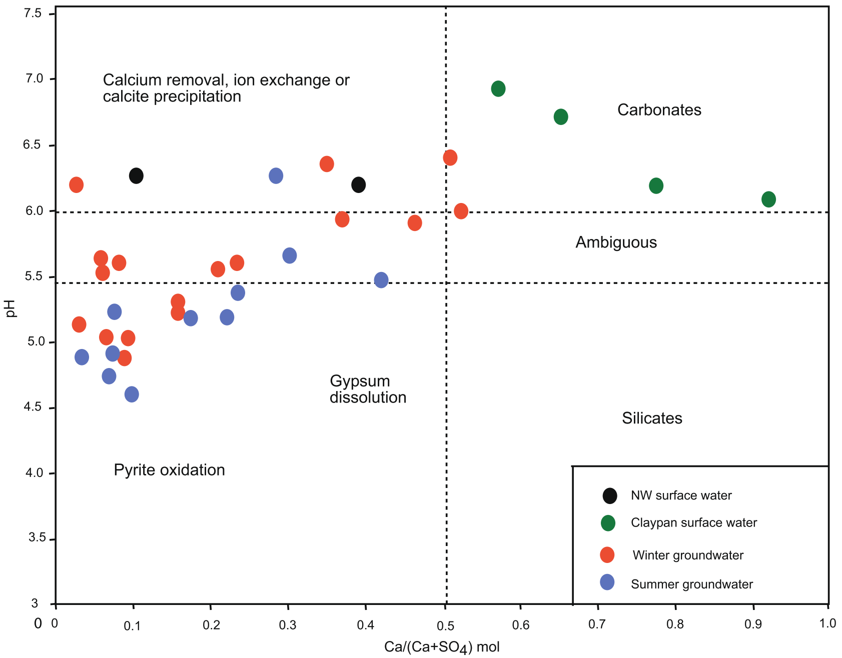

Fig. 8 Molar concentrations of Ca^{2+} and SO_4^{2-} expressed as Ca/(Ca+SO$_4$) vs. pH. Hounslow (1995) used this to examine the contributions from processes such as calcite precipitation, pyrite oxidation and gypsum dissolution to groundwater chemistry. Evident for DNR is that possibly all three are contributing

and Townley 2006) was used in this study. Comparisons of groundwater and surface water for the DNR with the Perth MWL indicates that the groundwater is likely derived from regional precipitation via surface water, which has accumulated over geologic time frames. Long term average $\delta^{18}O$ (−17.4‰) and δD (−3.85‰) for Perth rainfall (Turner and Townley 2006) lies between the DNR groundwater and surface-water data; however, it is similar to three surface and groundwaters sites in the northwest corner of the reserve. Both $\delta^{18}O$ and δD signatures for claypan surface waters are uniformly enriched compared to modern Perth rainfall. This is a perplexing situation given that evaporation is preferential towards ^{18}O enrichment compared to ^{2}H, even at 100% humidity (Kendall and Caldwell 1998). This suggests that there is likely some difference between a LMWL and the Perth MWL, which could only be proven by the compilation of a $\delta^{18}O$ and δD data base for rainfall samples collected around the DNR over numerous seasons.

Despite the lack of a LMWL, the $\delta^{18}O$ and δD dataset presented here provides significant insight into the hydrological functioning of the DNR. There appears to be no significant connection between the weathered bedrock aquifer and the sand aquifer and claypan surface waters, with possible very slow recharge to the weathered bedrock aquifer occurring. It can also be interpreted that the north western area of the reserve is a groundwater discharge zone, where shallow groundwater flows from the west and

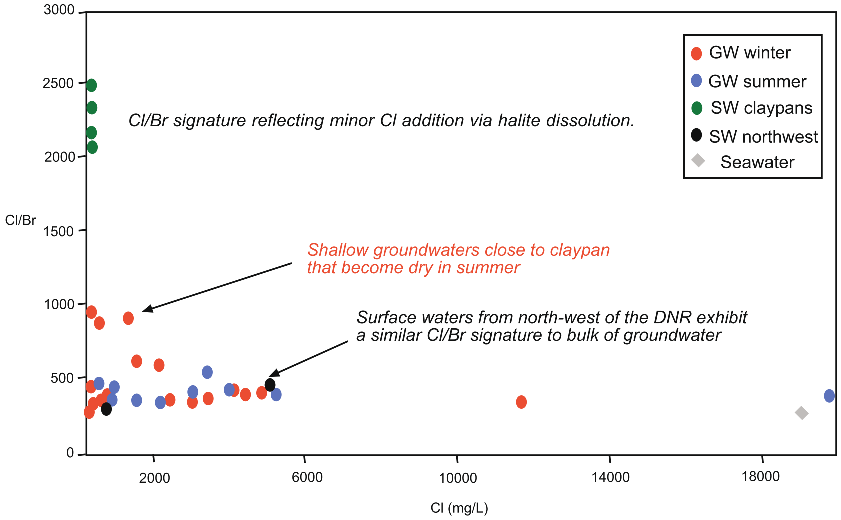

Fig. 9 Cl/Br ratios vs. Cl^{-} (mg/L) for surface waters (*SW*) and groundwaters (*GW*) for winter (September) 2008

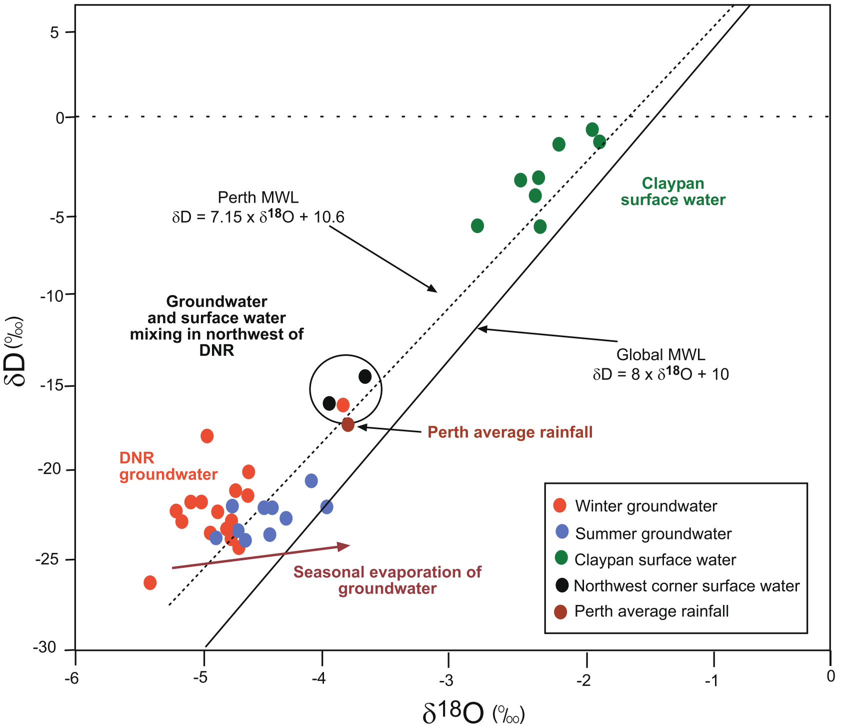

Fig. 10 $\delta^{18}O$ vs. δD data for surface waters and groundwaters for winter 2008 (September) and groundwaters for summer (May) 2009

expresses at the surface. These waters are in turn mixing with relatively recent rainfall additions. Furthermore, an indistinguishable variation in δD between summer and winter signatures combined with an enrichment of $\delta^{18}O$ for summer groundwaters indicates possible seasonal evaporation effects.

Nutrients

The concentration and distribution of TN (including nitrate and ammonium) and TP across the DNR provides an indication of nutrient fluxes and the threat such fluxes pose to biodiversity assets. TN values (>10 mg/L) for the southwest claypan surface water and subsurface waters close to the northeast claypan are well above the 4 mg/L threshold (Prober and Smith 2009) proposed for protection of native vegetation in the Western Australian wheatbelt. They are also surprisingly much higher than previously determined values (1.8– 2.3 mg/L; Cale 2005) and well in excess of the ANZEEC (2000) guidelines for aquatic wetland ecosystems (1.5 mg/L TN). These two TN contents are predominantly organic in composition, with little representation by $N\_NO_3^-$ or $N\_NH_3^+$. Hence, it's possible that these high organic TN contents reflect natural in-situ oxidation processes, which re-assimilate inorganic N to organic N (e.g., Heathwaite et al. 1996), and in turn concentrate them in the claypans. The significant variation in TN values within the claypans and surrounding areas indicates that the process is quite heterogeneous. Total phosphorous (TP) values determined for DNR claypan waters, including those with high TN, are much lower than the 5 mg/L threshold (Prober and Smith 2009) for native vegetation health in the Western Australian wheatbelt. However, one water sample from the southwest claypan (>0.3 mg/L) exceeds the ANZEEC (2000) guidelines (0.06 mg/L TP).

The clay dominance (>90%) within the freshwater claypan sediments indicates significant nutrient retention capabilities (Bowden et al. 1980). This is due to the high cation exchange capacities (CECs) of the two dominant minerals (Buol 2003), illite (10–40 cmol kg^{-1}), and kaolinite (3–15 cmol kg^{-1}). Thus the claypan sediments have significant ability to lock N and P into sediments. A previous study of Western Australia soils (Bettenay and Hingston 1964) found that clays with high illite content correlated with increasing levels of TN and TP.

Groundwater TN concentrations are greatest (>5 mg/L) along the western boundary of the DNR. Unlike the claypans this TN is dominated by inorganic N (predominantly nitrate), and exceed the 2 mg/L maximum threshold identified for many natural-state wetland systems (Shand and Edmunds 2008). They are also significantly higher than the nitrate levels identified for shallow (~1 mg/L) and deep (~0.1 mg/L) groundwater on the Darling Scarp Plateau, immediately west of the DNR (Donohue et al. 2001). High inorganic N concentrations in groundwater usually originate from agricultural fertiliser inputs, in the form of ammonium ($N\_NH_4^+$), which can via nitrification, be reduced to nitrate ($N\_NO_3^-$). Nitrate predominates in the DNR's high inorganic N groundwaters although; two groundwater samples (D8 and $D23_D$) are dominated by ammonium ($N\_NH_4^+$). These two also have summer ORP value indicative of reducing environments, which can restrict the nitrification process (thus halting the conversion of $N\_NH_3^-$ to $N\_NO_3^+$). The remainder exhibit ORP values that promote the nitrification process. Regardless of the form of the inorganic N in the western boundary groundwaters, their greater concentrations may be linked to the fertiliser regimes practiced on the agricultural lands situated immediately adjacent the reserve.

While the identification of elevated TN levels within the vicinity of the claypans is currently a cause for some concern, their organic and heterogenic nature suggests that they are of natural processes. For instance native species such as Acacia could be responsible for the fixation of N_2, which then accumulates in the clay rich sediments providing high TN concentrations in some places. N_2 fixing crops such as legumes planted in the adjacent agricultural lands can also increase TN and in turn via nitrification, ammonia and nitrate levels in soil (e.g., McNeill and Unkovich 2007), which may ultimately end up in groundwaters. Regardless of the source, it would appear that the southwest claypan owing to its proximity to the groundwaters along the western boundary of the DNR has some level of susceptibility to possible external nutrient inputs via surface flows or rising groundwaters. In comparison, the northeast claypan appears to be under no immediate threat from groundwaters with high inorganic N concentrations, due to its isolation from nearby agricultural areas. In order to assess the true nature of threats to the southwest claypan a more detailed investigation, in terms of seasonal and spatial variability, of N functioning is needed. Of further concern is that surface flows may be also nourishing invasive weed species and fostering their spread into the claypans. Species like Patterson's Curse (*Echium platagineum*), Wild gladiolus (*Gladiolus caryophyllaceus*), and blowfly and shivery grasses (*Briza* spp.) have been identified amongst the native biota (Keighery et al. 2002). While currently not widespread and confined to disturbed areas of the reserve (road edges, firebreaks and drainage lines from roads), their identification proximal to the southwest claypan is of an immediate concern.

Groundwater/surface-water interactions

The previously described isotopic and geochemical data suggests minimal connectivity between the surface waters and groundwaters throughout much of the DNR. However, there does appear to be some interaction between the claypan surface waters and the fringing shallow groundwaters (<5 m) of the sand aquifer. These fresh water flows appear mostly seasonal, entering the claypans from adjacent saturated sand deposits during the winter months. In the northwest region of the DNR, similar stable isotopic signatures for groundwaters and surface waters coincide with near-surface groundwater levels, indicating substantial hydrological connection between the two in that area. This connection is in the form of groundwater discharge at the break of slope, which is subsequently mixing with recent surface-water additions. The saline nature of these ephemeral surface waters in the northwest corner could be attributed to either to re-dissolved excess salt from the soil profile, or salt sourced from shallow groundwater. Two shallow bores ($D42_{OB}$ and $D42_{D}$) located in zone of groundwater recharge are relatively fresh suggesting the first option is more likely. Besides surface expression of shallow groundwater in the northwest corner, groundwater also flows further east into the north central area of the DNR. At this point it appears to be recharged to depth and also flowing northwards away from the DNR.

Hydrological threats to DNR

A future rise in the level of deep groundwater creating hydrological connectivity between it and the claypan subsurface and surface waters is a possible threat to the DNR claypans and their biota. Altered land management practices, larger watershed area, increased rainfall volumes, or a combination of all could drive such an alteration to the current hydrological state. The consequence is that large amounts of deep groundwater solutes such as Na^+ and Cl^- and possibly nutrients, could enter the surface and subsurface system in turn mixing with these fresher waters. Groundwater acidity could also become a problem if levels were to rise. Groundwater pH in the DNR is in the range that is regarded as common for the Western Australian wheatbelt (Degens et al. 2008); however, it is lower than the claypan surface waters. Hence these more acidic waters could potentially lower claypan surface-water pH and in turn impact biota should groundwater levels rise. It would appear that the potential for rising of poor quality groundwater is greatest around the southwest claypan due to the larger catchment area and exposure to cleared agricultural areas. In comparison, the northeast claypan is separated by bedrock highs from much of the DNR and agricultural lands and has a smaller catchment area.

While the threat from rising water tables should not be discounted, currently the key threat to the DNR is excess surface water. This water enters the fringes of the reserve during large and intensive rainfall events and has the potential to transport undesirable solutes (salt and nutrients) and weeds. The southwest claypan is at most threat due to its location on the DNR's periphery. This threat is not as significant for the northeast claypan due to its location further within the confines of the reserve. Furthermore the bedrock highs on its western and northern sides create a fringing groundwater divide that hydrologically isolates it from much of the DNR's western section. It is on the western side of this divide where groundwater flow from the west converges and vegetation death is apparent. The freshness of this groundwater and its shallow nature suggests that water logging and not salinity is the likely cause of the vegetation death, although other non-hydrological causes (e.g., *Phytophthora* die-back) may also be of concern in this area.

Conclusions

Hydrological and geochemical investigations of the Drummond Nature Reserve (DNR) presented in this study provide an understanding of the hydrological functioning of the reserve and its immediate surrounds. As a result, the processes related to altered hydrology, and their potential threat to the rare biota that currently exists within the reserve and its claypans has been appreciated. Biota associated with the southwest claypan is currently under considerable threat from weed invasion and the possibility of increasing anthropogenic nutrient loads originating from large episodic flows of surface water from adjacent agricultural lands. This threat in the southwest needs immediate monitoring and management, possibly surface-water diversion. In comparison, the threat from similar surface-water events to the northeast claypan is less likely due to a combination of its location deeper within the reserve and its hydrological confinement by bedrock highs.

Rising groundwater levels and the subsequent possibility of increasing salinity, nutrient loads or acidity does not appear to be a current problem for the claypans and their flora. However, the potential for alteration in the hydrological balance around the southwest claypan due to increasing surface-water inputs causing higher water tables should not be dismissed. This could create a hydrological connection between deeper groundwater and the shallow surface and subsurface waters that could impact associated biota. In the northwest area and along the northern boundary of the reserve, Wandoo and Banksia woodlands in sandy soils appear under threat from waterlogging due to a near-surface groundwater table. A more extensive drilling and geological mapping program is required across the DNR in order to confirm the extent of the bedrock high and subsequent effects on groundwater hydrology discussed here. The development of a robust water balance is needed to understand the exact role that surface water plays in the hydrological functioning of the DNR, in order to appreciate the frequency and volume of the surface flows, which have potential to transport nutrients and weeds. The construction of this water balance requires data such as precipitation, evaporation, transpiration, surface-water flows, and groundwater inflow and outflows. It also requires the collection of suitable time-frame-resolution groundwater levels and quality. Appropriate groundwater flow modelling would complement the water balance.

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References

Allison GB, Cook PG, Barnett SR, Walker GR, Jolly ID, Hughes MW (1990) Land clearance and river salinisation in the western Murray Basin. J Hydrol 264:170–184

Anand RR, de Broekert P (2005) Regolith landscape evolution across Australia: a compilation of regolith landscape case studies with regolith landscape evolution models. Cooperative Research Centre for Landscape Environments and Mineral Exploration, Canberra, Australia

ANZEEC (2000) Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Sydney

APHA (1995) Standard methods, 19th edn. American Public Health Association, Washington, DC

Appelo CAJ, Postma D (1993) Geochemistry, groundwater, and pollution. Balkema, Rotterdam, The Netherlands

Arad A, Evans R (1987) The hydrology, hydrochemistry and environmental isotopes of the Campase River aquifer system, North-Central Victoria, Australia. J Hydrol 95:63–86

Bennetts DA, Webb JA, Stone DJM, Hill DM (2006) Understanding the salinisation process for groundwater in an area of south-eastern Australia, using hydrochemical and isotopic evidence. J Hydrol 323:178–192

Bettenay E, Hingston FJ (1964) Development and distribution of soils in the Merredin area, Western Australia. Aust J Soil Res 2:173–86

Bowden JW, Posner AM, Quirk JP (1980) Adsorption and charging phenomena in variable charge soils. In: Theng BKG (ed) Soils with variable charge. New Zealand Society of Soil Science, Christchurch

Buol SW (2003) Soil genesis and classification. Blackwell, New York

Bureau of Meteorology (2010) Bureau of Meteorology climate data. http://www.bom.gov.au/. Cited 15 Jan 2010

Cale D (2005) Drummond Natural Diversity Recovery Catchment Aquatic Invertebrate Survey. Department of Conservation and Land Management Report, Perth, Australia

Carter JD, Lipple SL (1982)Moora, Western Australia 1:250 000 Geological Series: explanatory notes, sheet SH5OlO. Geological Survey of Western Australia, Perth, Australia

Cartwright I, Weaver TR, Fulton S, Nichol C, Reid M, Cheng X (2004) Hydrogeochemical and isotopic constraints on the origins of dryland salinity, Murray Basin, Victoria, Australia. App Geochem 19:1233–1254

Cartwright I, Weaver TR, Fifield K (2006) Cl/Br ratios and environmental isotopes as indicators of recharge variability and groundwater flow: an example from the southeast Murray Basin, Australia. Chem Geol 231:38–56

Chow W, Vogwill R, Forbes M (2010) Floristic values and hydrological threats to freshwater claypans in Drummond Nature Reserve, Western Australia. Aust Plant Conserv 18 (4):13–14

Clarke CJ, George RJ, Bell RW, Hatton TJ (2002) Dryland salinity in southwestern Australia: its origins, remedies, and future research directions. Aust J Soil Res 40:93–113

Commander DP, Schoknecht W, Verboom X, Casetta P (2001) The geology, physiography, and soils of wheatbelt valleys. In: Dealing with salinity in wheatbelt valleys: processes, prospects and practical options conference proceedings, Merredin, Australia, 30 July–1 August 2001

Correll DL, Jordan TE, Weller DE (1992) Nutrient flux in a landscape: effects of coastal land use and terrestrial community mosaic on nutrient transport to coastal waters. Estuaries 15 (4):431–442

Davis SN, Whittemore DO, Fabryka-Martin J (1998) Uses of chloride/bromide ratios in studies of potable water. Ground Water 36(2):338–350

Davis SN, Deayne CL, Zreda M, Moysey S (2001) Chlorine-36, bromide, and the origin of spring water. Chem Geol 179:3–16

Degens B, Shand P, Fitzpatrick R, George RG, Rogers S, Smith M (2008) Avon Basin, WA wheatbelt: an overview of geochemical risks of saline acid discharge from deep drains used to manage dryland salinity in Western Australia. In: Fitzpatrick R, Shand P (eds) Inland acid sulphate systems across Australia. CRC LEME open file report 249, CRC LEME, Canbrerra, Australia, pp 169–175

Deshon M (2000) Hydrological investigation and salinity risk within Drummond Nature Reserve. Department of Agriculture, Perth, Australia

Devito KJ, Dillon P (1993) The influence of hydrologic condition and peat oxia on the phosphorous and nitrogen dynamics of conifer swamp. Water Res Res 29:2675–2685

Donohue R, Davidson WA, Peters NE, Nelson S, Jakowyna B (2001) Trends in total phosphorous and total nitrogen concentrations of tributaries to the Swan-Canning Estuary 1987 to 1997. Hydrol Proc 15:2411–2434

Epstein S, Mayeda TK (1953) Variations of the 18O/16O ratio in natural waters. Geochim Cosmo Acta 4:213

Featherstone JM, Brown IM (1990) Industrial minerals. In: Geology and mineral resources of Western Australia. Memoir 3, Geological Survey of Western Australia, Perth

Feth JH (1981) Chloride in natural continental water: a review. US Geol Surv Water Suppl Pap 2176:30

George R, Clarke J, English P (2008) Modern and palaeogeographic trends in the salinisation of the Western Australian wheatbelt: a review. Aus J Soil Res 46:751–767

Hagedorn B, Cartwright I (2009) Climatic and lithologic controls on the temporal and spatial variability of CO_2 consumption via chemical weathering: an example from the Australian Victorian Alps. Chem Geol 260:234–253

Heathwaite AL, Johns PJ, Peters NE (1996) Trends in nutrients. Hydrol Proc 10:263–293

Herczeg AL, Edmunds WM (2000) Inorganic ions as tracers. In: Cook P, Herczeg AL (eds) Environmental tracers in subsurface hydrology. Kluwer, Boston

Herczeg AL, Torgersen T, Chivas AR, Habermehl MA (1991) Geochemistry of groundwaters from the Great Artesian Basin, Australia. J Hydrol 126:225–245

Herczeg AL, Simpson HJ, Mazor E (1993) Transport of soluble salts in a large semiarid basin: River Murray, Australia. J Hydrol 144:59–84

Hingston FJ, Gailitis V (1976) The geographic variation of salt precipitated over Western Australia. Aust J Soil Res 14:319–335

Hobbs RJ (1993) Effects of landscape fragmentation on ecosystem processes in the Western Australian wheatbelt. Biol Conserv 64:193–201

Horwitz P, Bradshaw D, Hopper S, Davies P, Froend R, Bradshaw F (2008) Hydrological change escalates risk of ecosystem stress in Australia's threatened biodiversity hotspot. J Royal Soc West Aust 91:1–11

Hounslow AW (1995) Water quality data, analysis and interpretation. Lewis, Washington, DC

Huston R, Mitchell D, Carter J, Keighery G (2000) Proposed Drummond Nature Reserve Natural Diversity Recovery Catchment. Department of Conservation and Land Management, Perth, Australia

Jolly ID, McEwan KL, Holland KL (2008) A review of groundwater-surface water interactions in arid/semi-arid wetlands and the consequences of salinity for wetland ecology. Ecohydrology 1:43–58

Kay T (2001) Solomon, Yulgan and Mt. Anvil catchment study, Western Australia: a hydrologeological and land degradation assessment. National Heritage Trust, Perth, Australia

Keighery GJ, Gibson N, Webb A, Muir WP (2002) A biological survey of the agricultural zone: vegetation and vascular flora of Drummond Nature Reserve. Cons Sci West Aust 4(1):63–78

Kendall C, Caldwell EA (1998) Isotope tracers in catchment hydrology. In: Kendall C, McDonnell JJ (eds) Fundamentals of isotope geochemistry. Elsevier, Amsterdam

Love AJ, Herczeg AL, Sampson L, Cresswell RG, Fifield LK (2006) Sources of chloride and implications for ^{36}Cl dating of old groundwater, southwestern Great Artesian Basin, Australia. Water Res Res 36:1561–1574

Marimuthu S, Reynolds DA, Le Gal LaSalle C (2005) A field study of hydraulic, geochemical and stable isotope relationships in a coastal wetlands system. J Hydrol 315:93–116

McArthur JM, Turner J, Lyons WB, Thirlwall MF (1989) Salt sources and water-rock interaction on the Yilgarn Blocks, Australia; isotopic and major element tracers. Appl Geochem 4(1):79–92

McNeill A, Unkovich M (2007) The nitrogen cycle in terrestrial ecosystems. Soil Biol 10(1):37–64

Moore DM, Reynolds RC Jr (1989) X-ray diffraction and the identification and analysis of clay minerals. Oxford University Press, Oxford

Pinder AM, Halse SA, McRae JM, Shiel RJ (2004) Occurrence of aquatic invertebrates of the Wheatbelt region of Western Australia in relation to salinity. Hydrobiology 543:1–24

Post V, Kooi H, Simmons C (2007) Using hydraulic head measurements in variable-density flow analyses. Ground Water 45 (6):664–671

PPK (2002) Groundwater and Salinity Investigation Solomon, Yulgan and Mt. Anvil Catchment: PPK Environment and Infrastructure, Perth, Australia

Prober SM, Smith FP (2009) Enhancing biodiversity persistence in intensively used agricultural landscapes: a synthesis of 30years of research in the Western Australia Wheatbelt. Agri Ecosys Environ 132(3–4):173–191

Rietveld HM (1969) A profile refinement method for nuclear and magnetic structures. J App Cryst 2:65–71

Rosen MR, Miser DE, Warren JK (1988) Sedimentology, mineralogy and isotopic analysis of Pellet Lake, Coorong region, South Australia. Sedimentology 38:102–112

Rosen MR, Turner JV, Coshell L, Gailitis V (1995) The effects of water temperature, stratification, and biological activity on the stable isotopic composition and timing of carbonate precipitation in a hypersaline lake. Geochim Cosmo Acta 59(5):979–990

Salama RB, Farrington P, Bartle GA, Watson GD (1993) The chemical evolution of groundwater in a first order catchment and the process of salt accumulation in the soil profile. J Hydrol 143(3–4):233–258

Schofield S, Jankowski J (2004) Hydrochemistry and isotopic composition of $Na–HCO_3$ rich groundwater from Ballimore region central New South Wales, Australia. Chem Geol 211:111–134

Shand P, Edmunds WM (2008) The baseline inorganic chemistry of European groundwaters. In: Edmunds WM, Shand P (eds) Natural groundwater quality. Blackwell, Oxford

Sharma MJ, Hughes MW (1985) Groundwater recharge estimation using chloride, deuterium and oxygen-18 profiles in the deep coastal sands of Western Australia. J Hydrol 81(1–2):93–109

Singh B, Sekhon GS (1979) Nitrate pollution of groundwater from farm use of nitrogen fertilizers: a review. Agri Environ 4:207–225

Turner JV, Townley LR (2006) Determination of groundwater flow-through regimes of shallow lakes and wetlands from numerical analysis of stable isotope and chloride tracer distribution pattern. J Hydrol 320:451–483

Ullman WJ (1995) The fate and accumulation of bromide during playa salt deposition: an example from Lake Frome, South Australia. Geochim Cosmo Acta 59:2175–2186

Wacey D, Wright DT, Boyce AJ (2007) A stable isotope study of microbial dolomite fractionation in the Coorong Region, South Australia. Chem Geol 244(1–2):155–174

Williams WD (1999) Salinisation: a major threat to water resources in the arid and semi-arid regions of the world. Lakes Res Res Manag 4:85–91