



Understanding the salinisation process for groundwater in an area of south-eastern Australia, using hydrochemical and isotopic evidence

D.A. Bennetts^{a,*}, J.A. Webb^{a,1}, D.J.M. Stone^{b,2}, D.M. Hill^{b,3}

^a*Department of Earth Sciences, La Trobe University, Vic. 3086, Australia*

^b*Environment Division, Australian Nuclear Science and Technology Organisation, PMB 1 Menai, NSW 2234, Australia*

Received 25 March 2004; revised 17 August 2005; accepted 19 August 2005

Abstract

Increases in groundwater salinity down gradient are a common occurrence in catchments throughout Australia, exacerbating the effects of dryland salinisation in discharge areas. Groundwater hydrochemical and isotopic data from the Willaura catchment in south-eastern Australia, which is affected by both primary (natural) and secondary (human-induced) salinity, allowed the factors that cause the down gradient trend in salinisation within this catchment to be determined. The overall salinity of the groundwater (0.8–70 mS/cm) is controlled by evapotranspiration, which concentrates cyclic salts in the unsaturated zone, greatly increasing the salinity of the soil–water to 3700–6400 mg/L Cl^- . The progressive addition of this saline soil–water to fresher groundwaters recharged on the catchment margins causes a gradual increase in salinity down gradient. The groundwater stable isotope compositions show that most recharge occurs in winter and spring. Groundwater salinities increase around the saline lakes of the discharge zone, due to direct evaporation from shallow watertables and minor dissolution of halite (as indicated by Cl^-/Br^- ratios). Mineral–water interactions within the aquifers cause a slight overall reduction in salinity; conversion of kaolinite to smectite and illite, and cation exchange of Na^+ for Ca^{2+} on smectites, cause Na^+/Cl^- , $\text{Mg}^{2+}/\text{Cl}^-$, K^+/Cl^- , Si/Cl^- and $\text{HCO}_3^-/\text{Cl}^-$ ratios to progressively decline and pH to gradually increase down gradient. Oxidation of organic matter causes a strong decrease in the redox potential of the groundwaters down gradient. The groundwater ages increase from modern (containing tritium) on the catchment margins to ~8000 years (based on ^{14}C dating) at the end of the ~25 km flow path. The older groundwaters are isotopically heavier than the younger waters, probably due to recharge during a wetter climate in the early Holocene. The groundwater ages show clearly that the progressive addition of saline soil–water, causing groundwaters to become more saline down gradient,

* Corresponding author. Tel.: +61 3 9690 0522; fax: +61 3 9690 0585.

E-mail addresses: darren.bennetts@pjra.com.au (D.A. Bennetts), john.webb@latrobe.edu.au (J.A. Webb), dms@ansto.gov.au (D.J.M. Stone), dmh@ansto.gov.au (D.M. Hill).

¹ Fax: +61 3 9479 1272.

² Fax: +61 2 9717 9260.

³ Fax: +61 2 9717 9286.

has occurred throughout the Holocene and may explain the occurrence of primary salinisation within many Australian catchments.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Salinity; Hydrochemistry; Hydrogeology; Stable isotopes; Radiocarbon; Tritium

1. Introduction

Australia is the driest inhabited continent, and groundwaters throughout the country are often saline and dominated by Na^+ and Cl^- (e.g. Arad and Evans, 1987; Herczeg et al., 1991; Salama et al., 1993a). The salinisation of groundwater, surface water and soils in non-irrigated environments (dryland salinity) is a major environmental and economic problem across large areas of Australia (Ghassemi et al., 1995). Within catchments affected by dryland salinity, groundwaters typically show increasing salinity down gradient (e.g. Arad and Evans, 1987; Bennetts and Webb, 2004; De Deckker, 2003; Herczeg et al., 1991; 2001; Komarower and Wall, 1979; Macumber, 1991; Salama et al., 1993a; Dogramaci et al., 1998; Salama et al., 1999; Schofield and Jankowski, 2003; Cartwright et al., 2004), exacerbating salinisation in groundwater discharge zones. Although these saline groundwaters have been the subject of considerable study, the chemical evolution that causes the down gradient increase in salinity is not well understood. Furthermore, the relative contribution to the salinity increase of mineral–water reactions, including silicate weathering and clay transformation, has not been well documented.

This study investigates the processes controlling the down gradient increase in groundwater salinity in Australia through a detailed examination, using hydrochemical and isotopic methods, of the Willaura catchment in south-western Victoria, south-eastern Australia. This lies within the Glenelg–Hopkins regional catchment, which contains a large area (144,500 ha) affected by dryland salinity, predicted by the (Australian) National Land and Water Resources Audit (2001) to increase up to six times by 2050. The Willaura catchment is of particular importance because the large proportion of salinized land that may further expand threatens local agriculture and important wetlands used by migratory

birds (Glenelg Hopkins Regional Catchment Strategy, 2003).

2. Catchment characteristics

2.1. Geomorphology

The Willaura catchment is ~85,000 ha in area, and comprises a gently undulating and south-sloping plain of approximately 260 m elevation, bordered to the east by the Hopkins River and to the west by the Grampians Ranges (Fig. 1), which rise almost 500 m above the plain. Incised streams flowing southeast from the Grampians Ranges terminate in large freshwater lakes (Lake Muirhead, Mt William Swamp and The Morass) nestling against the north-west margin of the Plio-Pleistocene basalts in the area (Fig. 1). These lakes have been part of this landscape throughout much of the Quaternary (Street et al., 1988), and formed when basalt lavas blocked streams flowing from the Grampians Ranges into the Hopkins River (Hills, 1975).

In the south of the catchment is the Stavely Range; north of this the saline Cockajemmy Lakes run east–west in a topographic low along the southern edge of the Plio-Pleistocene basalt flows, and step down towards the east (Fig. 1). The lakes generally dry out in summer, leaving a thick crust of halite precipitate, and fill again with the onset of winter.

There is no surface flow from any of the lakes to the Hopkins River to the east; the Willaura catchment is an entirely enclosed surface drainage basin.

2.2. Vegetation and landuse

The indigenous vegetation comprised River Red Gums along the Hopkins River, She-Oaks on the Stavely Range, and an almost treeless central plain of deep-rooted perennial grasses (Mitchell, 1839). Much of this was progressively cleared after 1846, creating

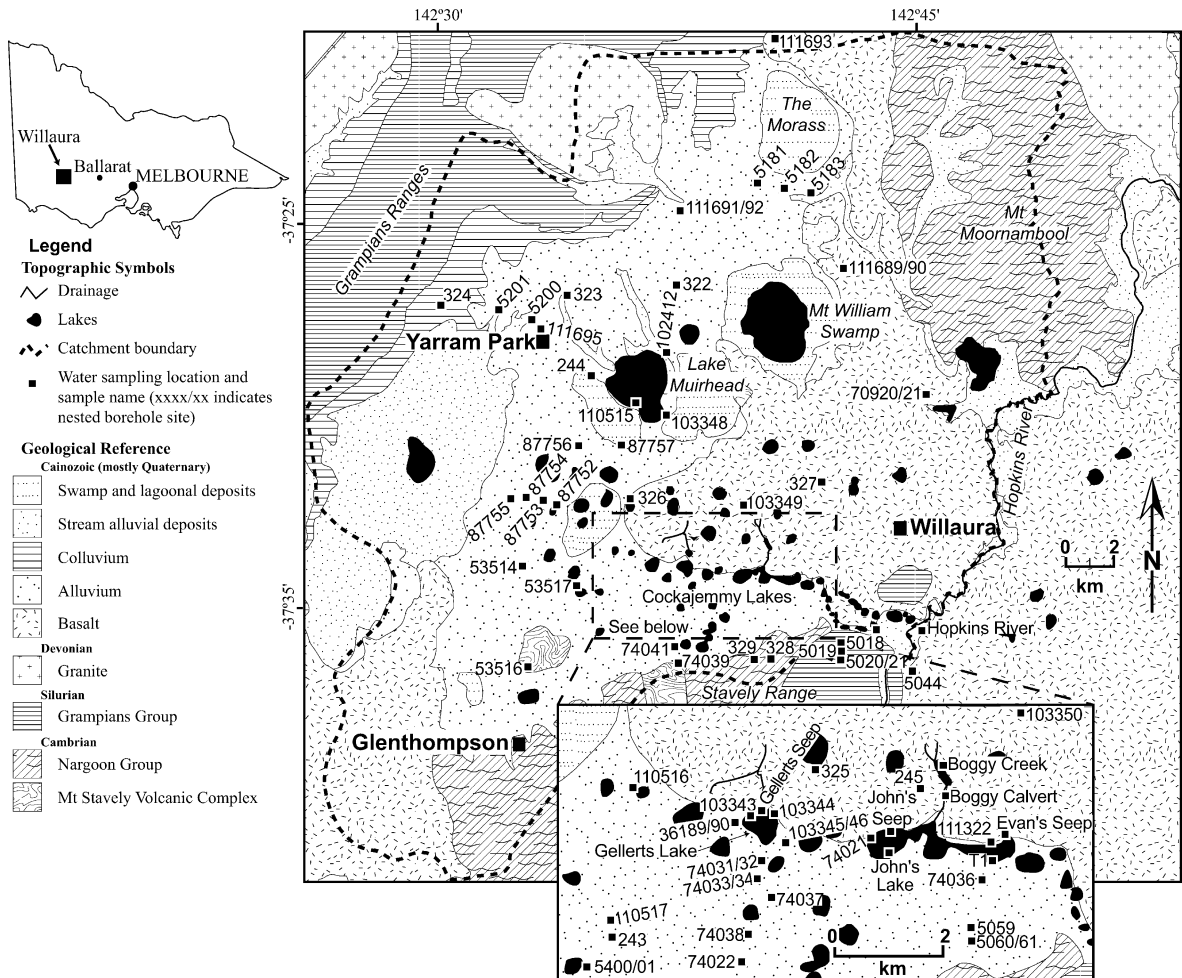


Fig. 1. Map of Willaura catchment showing sampling localities.

agricultural grassland, except for small areas of remnant native forest in the northwest along the slopes of the Grampians Ranges (Mann and Nolan, 1989). Currently the area is cropped for wheat, oats and canola, and used for sheep grazing.

2.3. Climate

Rainfall over the catchment decreases from west to east, from over 1000 mm in the Grampians Ranges to 613 (± 135 SD) mm at Yarram Park in the centre of the catchment and 545 (± 105 SD) mm at Willaura in the east (data from Bureau of Meteorology, Australia).

Maximum rainfall is received over winter, and exceeds or equals evaporation from May to

September; the peak period of winter rainfall is June to September, when groundwater recharge is most likely to occur. Pan evaporation from the nearest weather station at Hamilton, ~ 40 km southwest of the study area, is highest from December to February and averages 1350 mm annually (data from Bureau of Meteorology, Australia). Average temperatures are 26–28 °C in summer and 4–12 °C in winter, and humidity (at 3 pm) averages 56% (data from Bureau of Meteorology, Australia).

2.4. History of salinisation

Natural (primary) salinity has long been a prominent feature of the landscape in the Willaura

catchment, and was first documented by Major Mitchell in 1836: “I was somewhat surprised to find after encamping, that the water in the adjacent lakes [Cockajemmy Lakes] was extremely salty” (Mitchell, 1839). However, the Willaura catchment has suffered an increase in salinisation since broad-scale landuse change (i.e. clearing). This secondary salinisation has occurred through rising watertables and increased groundwater discharge, resulting in higher lake levels, particularly in the Cockajemmy Lakes, increased salinity in pre-existing saline lakes and the emergence of new saline scalds in topographic lows and drainage lines (Mann and Nolan, 1989).

3. Geology and hydrogeology

Three major aquifers are present in the Willaura area. Cambrian greenstones and turbidites (Mt Stavely Volcanic Complex and Nargoon Group respectively; VandenBerg et al., 2000) and Silurian sandstones (Grampians Group; Cayley and Taylor, 1997) together form a major regional aquifer (referred to here as the Palaeozoic basement aquifer) beneath the study area. The greenstones are largely andesitic–dacitic lavas, tuffs and volcanoclastic sandstones (Buckland, 1986); the Nargoon Group comprises sandstone with minor siltstone and calcareous mudstone, whilst the Grampians Group contains quartzose and feldspathic sandstone with minor conglomerate (Cayley and Taylor, 1997). The Palaeozoic basement is fracture-dominated, possessing almost no primary porosity. It is typically confined, except for outcrops in the Grampians Ranges, Mt Moornambool and Stavely Range (Fig. 1). Soils developed on the basement exposures are generally sandy and permeable, particularly on the Silurian sandstones of the Grampians Ranges, and often overlie deep weathering profiles (Camilleri, 1999).

The second major aquifer comprises colluvium on the flanks of the Grampians Ranges and alluvial sediments in the centre of the catchment (grouped together here as the alluvial aquifer). This aquifer is typically unconfined, except where overlain by Plio-Pleistocene basalt (Fig. 1), and directly underlies most of the lakes of the catchment; alluvium is up to 30 m thick beneath the Cockajemmy Lakes. These

sediments are variably consolidated with moderate intergranular porosity, and are dominantly composed of clay, silt and sand on the central plain, and clay, sand and cobbles on the flanks of the range (Stuart-Smith and Black, 1999; Buckland, 1986). Their age is thought to span from the Eocene to the Quaternary (Mann et al., 1992; Stanley, 1983). The older Tertiary sediments are strongly ferruginised, and are covered by a thin veneer of Quaternary alluvium, except where they underlie the basalt aquifer in the south of the catchment. Duplex clay soils are developed on surface exposures of the alluvium (Sibley, 1967).

The third aquifer comprises Plio-Pleistocene basalts of the Newer Volcanics, which cover most of the eastern part of the catchment, overlying the alluvial and Palaeozoic basement aquifers, with an average thickness of 30–40 m (Cayley and Taylor, 1997). A restricted palaeovalley intersected in borehole 327 (Fig. 1) contains basalts 64 m thick, representing at least three different flows separated by palaeosols up to 7 m in thickness. Soils on the basalts are typically clay-rich duplex profiles, similar to those on the alluvium, with a bleached yellow B-horizon (Sibley, 1967).

Groundwater flow, based on potentiometric data from the present study and Williams (1997), is from the catchment margins to the north and north-west (predominantly the Grampians Ranges) towards the south-east, ultimately terminating in saline springs (Gellerts Seep, Johns Seep and Boggy Creek spring) on the margins of the Cockajemmy Lakes, about 25 km from the dominant recharge areas. Groundwater also flows northwards into these lakes from the Stavely Range, although this is relatively minor and not discussed further.

4. Methods

Sixty-nine groundwater observation boreholes and surface waters were sampled three times for EC, pH, redox and temperature measurements over an 18-month period (May 2000–June 2001). Thirty-eight boreholes and five surface water sites were also sampled for major element analysis; samples were filtered through 0.45 µm filter paper and stored at < 4 °C. Alkalinity was determined by standard titration with HCl, with further anions being analysed by HPLC at CSIRO, Clayton. Cations were determined

Table 1
Median composition of Willaura groundwater and ionic (mass) ratios, with comparison to those for seawater (Drever, 1997) and local rainfall (Bormann, 2004)

Median (mg/L)	EC (mS/cm)	Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺	Si	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	NO ₃ ⁻	Br ⁻	pH	Na ⁺ /Cl ⁻	Ca ²⁺ /Cl ⁻	Mg ²⁺ /Cl ⁻	K ⁺ /Cl ⁻	Si/Cl	SO ₄ ²⁻ /Cl ⁻	HCO ₃ ⁻ /Cl ⁻	NO ₃ ⁻ /Cl ⁻
Seawater ^a	54171	10770	412	1290	380	2	19500	2715	142	-	-	-	0.55	0.021	0.066	0.019	0.0001	0.14	0.007	-
Local rain-fall ^b (n=6)	-	2.8	0.6	0.4	0.2	-	4.3	-	2.5	-	-	-	0.65	0.141	0.094	0.047	-	-	0.576	-
Rainfall south-eastern Australia ^c (n=51)	-	1.3	0.8	0.3	0.2	1.4	1.4	0.8	2.4	-	-	-	0.79	0.339	0.171	0.105	-	0.50	1.143	-
Alluvial aquifer (n=12)	17.3	2310	223	377	49	8	6039	465	208	40	23	7.4	0.40	0.036	0.070	0.009	0.0017	0.10	0.037	0.008
Basalt (n=5)	12.7	1134	207	226	54	8	3067	257	334	38	16	7.5	0.40	0.058	0.074	0.015	0.0024	0.10	0.050	0.008
Palaeozoic basement (n=18)	14.4	2877	272	488	70	7	5610	974	220	9	27	7.2	0.52	0.048	0.078	0.016	0.0017	0.16	0.039	0.001
Overall (bores; n=35)	13.2	2289	248	410	54	8	5870	729	244	9	24	7.4	0.41	0.040	0.070	0.009	0.0017	0.11	0.049	0.002

^a Drever (1997).

^b Cavendish, VIC (Hutton and Leslie, 1958).

^c Combined data from Hutton and Leslie (1958); Blackburn and McLeod (1983).

on acidified samples (1% HNO₃) by ICP-OES and AAS at La Trobe University. Six borehole and five surface water samples were analysed for δ¹⁸O and δ²H at Monash University using the method described by Cartwright et al. (2004); several of these sites were sampled for stable isotope analysis three times over the period May 2000 to June 2001. Twelve tritium and three ¹⁴C ages were determined on 1 L samples collected in cleaned (HNO₃) glass bottles at ANSTO, Sydney, using the method of Lawson et al. (2000) for ¹⁴C determination. Soil–water Cl⁻ concentrations were determined on 1:5 soil–water extracts taken from 3 m cores, sampled at 10 cm intervals, drilled adjacent to pre-existing observation boreholes and refrigerated upon collection.

5. Chemical evolution of Willaura groundwaters

5.1. General groundwater characteristics

The groundwater composition is relatively homogenous; all samples are NaCl dominated (almost 80% of TDS), and salinity (as EC) and Cl⁻ are very strongly correlated ($r^2=0.98$). Mg²⁺ and SO₄²⁻ are typically more abundant than Ca²⁺ and HCO₃⁻; Si and K⁺ are minor phases, and NO₃⁻ and Br⁻ are variable and frequently below detection limit. The pH values are circum-neutral (5.1–8.78) and Eh values vary from oxidising in recharge areas (up to 218 mV) to strongly reducing down gradient (–138 mV). Groundwater temperatures range from 15 to 22 °C, several degrees warmer than the mean daily air temperature (~19 °C in summer and ~8 °C in winter; data from Bureau of Meteorology, Australia), and probably reflect warming by a combination of solar radiation and geothermal heat (Vaught, 1980).

The major element composition is consistent with a cyclic origin (rainfall and/or windblown dust) for the dissolved solutes. ³⁶Cl/Cl⁻ ratios in groundwater from basalt and alluvial aquifers ~50 km to the south-west of Willaura show no identifiable contribution to the Cl⁻ content of the groundwater from rock weathering or connate water in the aquifer sediments (Bennetts and Webb, 2004). In addition, ¹⁴C estimates of groundwater residence time (see later discussion) are over four orders of magnitude younger

than the Cambrian and Silurian marine sediments within the study area, indicating that any connate water would have long been removed. Cl^-/Br^- ratios (Table 1) approximate those in modern precipitation, consistent with a cyclic origin for these ions (Davis et al., 1998); the lowest ratios occur in groundwaters near the saline Cockajemmy Lakes, indicating a minor influence from dissolution of halite in the lakebeds.

5.2. Salinity increase down gradient

Groundwater salinity increases down gradient in all three aquifers in the study area (Fig. 2). Because salinity and Cl^- concentration are very strongly correlated, and Cl^- is chemically inert and not involved in chemical reactions in the aquifer, the down gradient increase in salinity is not due to mineral–water interactions within the aquifers.

In the Palaeozoic basement and alluvial aquifers, recharge predominantly occurs through the slopes along the catchment margins (in particular the Grampians Ranges), where groundwaters are freshest (minimum 0.8 mS/cm). The soils are typically thin and sandy, allowing rapid recharge and thereby limiting the degree to which infiltrating water is concentrated by evapotranspiration. However, across the central plain, surface recharge to the alluvial and basalt aquifers occurs diffusely through clay-rich

soils. Infiltration through these soils is typically slow, and strong evapotranspiration forms an intermediate reservoir of saline soil–water in the unsaturated zone. Median soil–water Cl^- contents measured below the root zone across the central plain range between 3700 and 6400 mg/L. High salinity soil–water occurs near the root zone in many Australian catchments, and the link between saline soil–water and high rates of transpiration is well established (e.g. Leaney et al., 2003; Mazor and George, 1992; Turner et al., 1987).

Groundwaters in the alluvial aquifer and the upper layers of the basalt display concordant down gradient increases in salinity (the latter aquifer is mainly recharged by lateral flow from the adjacent alluvium). This progressive salinisation of both aquifers is due to mixing between low salinity soil–waters recharged on the catchment margins and high salinity soil–waters of the central plain (Fig. 2). All groundwater samples, except those immediately surrounding the saline Cockajemmy Lakes (discussed below), plot on a mixing line between these two end-members ($r^2 = 0.47$). As groundwater flows through the alluvial and upper basalt aquifers, it accumulates saline water infiltrating downwards from the soils above. Hence, the increasing groundwater salinities within the basalt and alluvial aquifers are limited by the maximum salinity of the soil–water, and so cannot exceed 6400 mg/L Cl^- (~ 17 mS/cm; Fig. 2) unless affected by another process (e.g. evaporation).

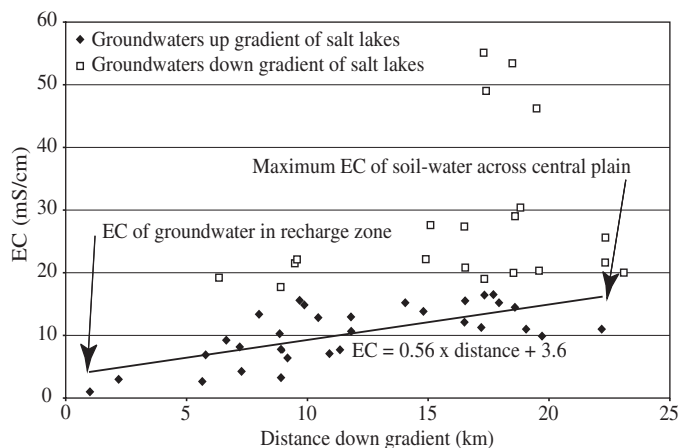


Fig. 2. Salinity (EC) evolution down gradient. Distances down gradient are measured from recharge area to borehole location perpendicular to potentiometric surface contours from Williams (1997).

Groundwaters in the underlying Palaeozoic basement aquifer are typically fresher than those in the overlying alluvium and basalts, e.g. half as saline at the nested boreholes 70920/70921 (Fig. 1), and display a more subtle increase in salinity down gradient. Fresh groundwater, recharged through outcrops on the catchment margins, particularly in the Grampians Ranges, mixes down gradient with saline groundwaters leaking from the overlying basalt and alluvial aquifers.

Groundwaters from the deepest, valley-filling part of the basalt (borehole 327) are substantially fresher and much older (~8000 years; see later discussion) than shallow groundwater in the basalt aquifer. Clay-rich palaeosols within the basalt sequence probably act as semipermeable aquitards separating the deep and shallow groundwater. The deeper parts of the basalt aquifer within the palaeovalley are recharged by lateral flow of relatively fresh groundwater from the surrounding Palaeozoic basement, and therefore form part of the basement regional groundwater flow system.

Groundwaters located adjacent to the saline Cockajemmy Lakes, at the end of the groundwater flow path in the Willaura catchment (Fig. 1), have salinities of 18–70 mS/cm, greater than expected from progressive additions of saline soil–water (Fig. 2), indicating there are other processes active here. Watertables in this area are relatively close to the surface (generally <2 m; Williams, 1997) so that direct evaporation of the groundwater can occur, resulting in very high soil–water Cl^- concentrations (17,000–25,000 mg/L Cl^- ; ~50–70 mS/cm). In addition, the waters of Cockajemmy Lakes are very saline (up to 645 mS/cm) and have enriched $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures (see later discussion) as a result of direct evaporation. Most evaporation of lake waters occurs over summer, forming dense plumes of saline groundwater that sink into the directly underlying alluvial aquifer. Thus groundwater in borehole 74021, which lies down gradient of the very saline Gellerts Lake (Fig. 1), increased in salinity from 23 mS/cm in April 2001 to 70 mS/cm in June 2001, as the lake water evaporated in summer made its way through the aquifer; similar processes have been identified at numerous salt lakes throughout southern Australia (e.g. Jones et al., 1994; Macumber, 1992; Rosen et al., 1996; Simmons and Narayan, 1998; Swane et al., 2001). The groundwater hydraulic gradient around Cockajemmy Lakes indicates that the highly saline waters then move east toward the Hopkins River, where

saline groundwater intrusions have been identified (Price, 1994). The increasing salinisation of the Cockajemmy Lakes may therefore be partly responsible for the currently rising salinity of the Hopkins River (0.0735 mS/cm/year; Smith and Nathan, 1999).

Down gradient increases in groundwater salinity similar to those at Willaura occur in a variety of groundwater systems within Australia (e.g. Arad and Evans, 1987; Macumber, 1991; Salama et al., 1993b). Similar examples have also been recorded from USA, Sudan, Canada (Salama et al., 1999), England (Elliot et al., 1999), Tunisia and Algeria (Edmunds et al., 2003), where a combination of evaporation in discharge zones and connate salt dissolution explains the down gradient salinity increases. In Australia considerable salt concentration by direct evaporation may occur in discharge zones (Jenkin and Dyson, 1983; Cartwright et al., 2004), but connate salt and evaporites are not important, because cyclic salts are the dominant salt source, with minor influence from water–rock interaction (e.g. Cartwright et al., 2004). Rather most Australian studies have suggested that increased groundwater salinity is due to clearing of native forests, resulting in enhanced recharge, which either leaches salt downward from salt stores in the unsaturated zone (e.g. Arad and Evans, 1987; Jenkin and Dyson, 1983; Leaney et al., 2003) or causes the watertable to rise, dissolving salt within the soil as it does so (Macumber, 1991). In addition, differing palaeo-recharge rates may influence the down gradient trend (Herczeg et al., 2001), and Love et al. (1994) suggested that this could cause salinity to rise from 500 to 3000 mg/L along a ~50 km flow path.

None of the above reasons put forward for studies elsewhere in Australia and other places can completely explain the groundwater salinity trends at Willaura. Adjacent to the groundwater discharge zone of the saline Cockajemmy Lakes, evaporation and leaching of soil salt by rising watertables are undoubtedly increasing the groundwater salinity, but these processes cannot influence deeper groundwaters throughout the remainder of the catchment. Furthermore, the down gradient increase in salinity occurs in waters thousands of years old (see later discussion), whereas enhanced recharge due to clearing of native forests has maximum direct influence on only the youngest groundwaters. Changing palaeo-recharge rates may have had an impact on Willaura

groundwater, but the effects are small compared to the salinity increases observed (Fig. 2). In contrast, the explanation proposed here, i.e. that as groundwater flows down gradient it receives a cumulatively greater input of saline water infiltrating from the soil above, accounts for the development of down gradient increases in salinity prior to land-use change (primary salinity) in unconfined aquifers, and leakage from unconfined into underlying confined aquifers can impose the same salinity increase on the deeper groundwater. The fact that down gradient primary salinisation has been identified in many confined and unconfined aquifers throughout Australia suggests that this mechanism probably applies (in combination with secondary processes like evaporation) to other Australian catchments.

5.3. Interactions between groundwater and aquifers

Although water–rock interactions are not the main cause of the down gradient increase in groundwater salinity, they nevertheless influence the groundwater composition, and their relative effect can be gauged by comparing the median groundwater composition with that of local rainfall, using the chemically inert species Cl^- . The Cl^- mass concentration of local rainfall (Table 1) was standardised to the median Cl^- mass content of the Willaura groundwaters, and this standardisation factor applied to all species in the rainwater (Table 1). The median Willaura groundwater (9607 mg/L of Cl^- , Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Si and SO_4^{2-}) is 40% less than the standardised rainfall composition on a mass basis (15,949 mg/L of the same ions); Na^+ , Ca^{2+} , Mg^{2+} , K^+ and Si have been removed by water–rock interaction within the aquifers (discussed further below). Thus mineral–water reactions within the aquifers in the Willaura catchment cause a moderate reduction in groundwater salinity, and subsequently the major influence on groundwater composition is the evapotranspiration of rainfall. The comparison is believed to be valid because ion/ Cl^- ratios in Willaura rainfall are likely to have been more or less the same over the Holocene, as the main process affecting rainwater composition in this area, incorporation of seaspray (Bormann, 2004), is unlikely to have changed over this time. The water–rock reactions involved will now be discussed in turn.

5.3.1. Silicate mineral weathering

Weathering of pyroxene, plagioclase and olivine in the basalt aquifer elevates groundwater $\text{HCO}_3^-/\text{Cl}^-$, $\text{Ca}^{2+}/\text{Cl}^-$ and Si/Cl^- ratios above those in groundwaters within the basement and alluvial aquifers (Table 1). $\text{Mg}^{2+}/\text{Cl}^-$ and Na^+/Cl^- ratios in the basalt groundwaters should also be increased by these weathering reactions, but are not dissimilar to those in groundwater in the other aquifers (Table 1), suggesting that Mg^{2+} and Na^+ are being removed (see below). The Palaeozoic basement and alluvial aquifers contain few reactive silicate minerals (Cayley and Taylor, 1997), apart from the andesitic–dacitic greenstones within the basement, which have a limited influence because they are uncommon and relatively impermeable.

5.3.2. Interaction with clays

Na^+/Cl^- , K^+/Cl^- , Si/Cl^- and $\text{Mg}^{2+}/\text{Cl}^-$ ratios demonstrate a progressive decline down gradient, whereas $\text{Ca}^{2+}/\text{Cl}^-$ shows no trend and pH increases. Ion/ Cl^- mass ratios of all the above species are well below those in modern precipitation in the area (Table 1), indicating that water–mineral reactions within the aquifers are removing these ions from solution and therefore, overall, reducing groundwater salinity.

The K^+ reduction is probably due to the formation of illites; this process has been identified as a significant sink for K^+ elsewhere in Australia (McArthur et al., 1989; Salama et al., 1993a,b). X-ray diffraction analyses show that illite is a dominant constituent of the alluvium and soils on the basalt and alluvial aquifers.

Na^+ , Si, Mg^{2+} and Ca^{2+} are probably being consumed by the conversion of kaolinite to smectite, because the freshest Willaura groundwaters plot within the kaolinite stability field, with a general progression to smectite down gradient (Fig. 3). This is a common reaction in aquifers throughout Australia (e.g. Blake, 1989; Herczeg et al., 1991). The decline in Na^+/Cl^- , $\text{Mg}^{2+}/\text{Cl}^-$, $\text{HCO}_3^-/\text{Cl}^-$ and Si/Cl^- ratios down gradient indicates that the amount of these ions released in silicate weathering reactions is less than that consumed by smectite formation. In contrast, $\text{Ca}^{2+}/\text{Cl}^-$ ratios display no significant trend down gradient, indicating there is another process adding Ca^{2+} , and pH values increase markedly down gradient

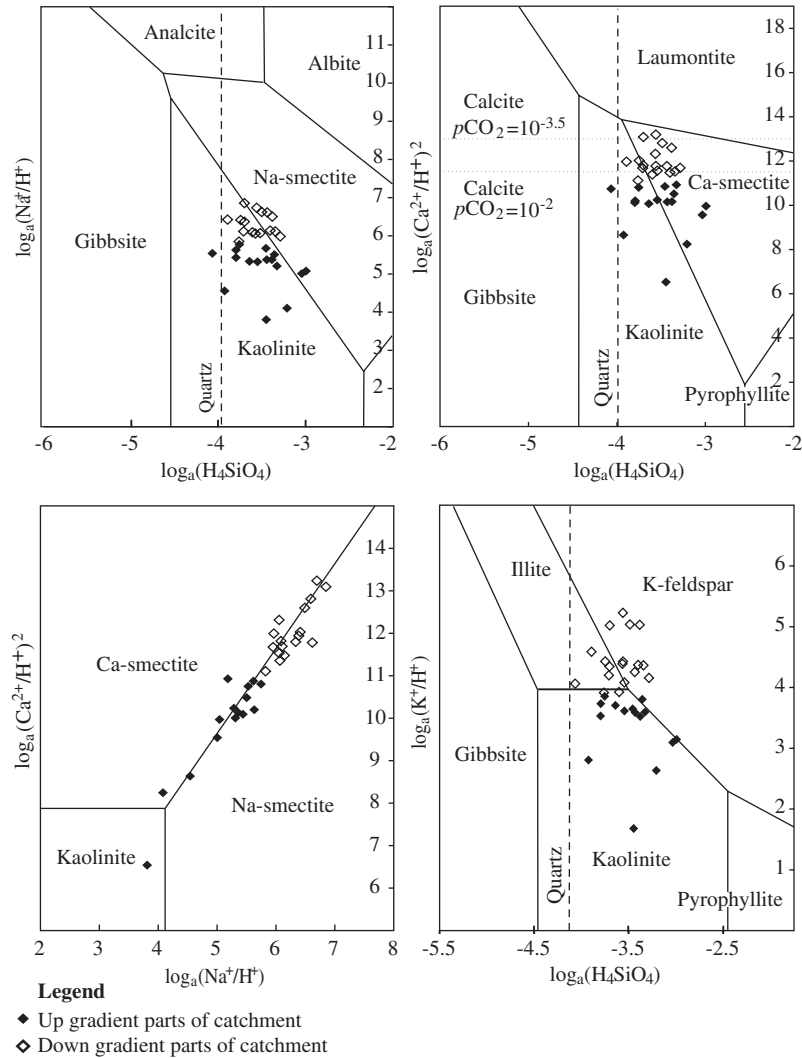


Fig. 3. Willaura groundwater compositions plotted on mineral diagrams for the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system, $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system and $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system, all at 25 °C and 1 atm (after Drever, 1997).

($r^2=0.6$ for pH versus distance down gradient). Cation exchange on the smectites is most likely responsible, whereby Ca^{2+} is replaced by Na^+ and H^+ , producing the observed gain in Ca^{2+} , loss of Na^+ and increase in pH down gradient. The removal of H^+ by this reaction is greater than the production of H^+ during the conversion of kaolinite to smectite, so $\text{Na}^+/\text{Ca}^{2+}$ exchange on smectites controls the Willaura groundwater pH. This process has also been recorded influencing saline groundwaters in northern Victoria (Arad and Evans, 1987) and New South Wales

(Jankowski and Acworth, 1993). Calcite dissolution is not involved, since there is no calcite known in the aquifers, and groundwater $\delta^{13}\text{C}$ values are indicative of biogenic rather than calcitic carbon (see later discussion).

5.3.3. Organic matter oxidation

The redox potential decreases down gradient, particularly in the alluvial aquifer ($r^2=0.47$ for Eh versus distance down gradient), from 121 to 218 mV in the northwest recharge areas to -138 mV at

Gellerts Seep at the Cockajemmy Lakes. The decrease is largely due to reaction with organic matter; two-thirds of the boreholes with reducing waters are screened in the alluvial aquifer, which commonly contains ligneous beds (Mann and Nolan, 1989), and organic matter was present in several groundwater samples. Some groundwaters in the basalt have negative redox values, most likely due to recharge through the overlying clay-rich soils, which become waterlogged and reducing in winter due to their low permeability (Sibley, 1967).

Boreholes 243 and 327 lie well down gradient yet have oxidising, relatively fresh groundwaters, because they screen deep aquifers (Palaeozoic bedrock and basalt) with little or no organic matter, recharged rapidly through thin, sandy soils on the slopes of the Grampians Ranges with minimal input of reduced, saline soil–water.

5.3.4. Sulphide oxidation

The Palaeozoic basement contains appreciable amounts of framboidal pyrite (Joplin, 1963), and pyrite oxidation is probably responsible for the relatively high groundwater $\text{SO}_4^{2-}/\text{Cl}^-$ ratios in this aquifer (Table 1) and their increase down gradient. The decrease in redox potential down gradient may also be partly due to pyrite oxidation. Nevertheless, the groundwater $\text{SO}_4^{2-}/\text{Cl}^-$ mass ratios at Willaura (median 0.12) are substantially less than in aquifers where pyrite oxidation is a major influence (e.g. 0.35; Jankowski and Acworth, 1993). Furthermore, this reaction releases acidity, yet the pH rises down gradient.

6. Stable isotope evolution of Willaura groundwater

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ compositions of Willaura groundwater samples plot close to the meteoric water line (MWL) for Adelaide (nearest IAEA/WMO meteorological station, 450 km west of Willaura; Fig. 4), indicating that the groundwaters are of meteoric origin and not significantly affected by open water or unsaturated zone evaporation (Allison et al., 1984; Drever, 1997). Most groundwaters have a very similar composition to the average winter rainfall at Adelaide (-5.1‰ , -27.9‰), suggesting that the majority of recharge in the Willaura catchment occurs

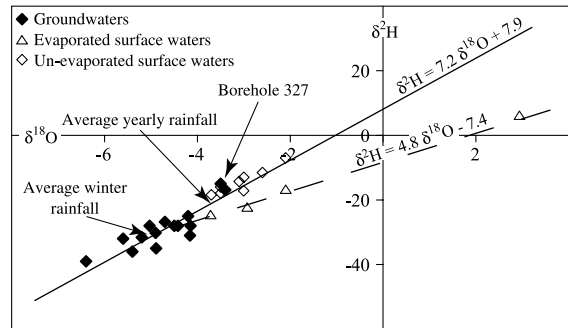


Fig. 4. Stable isotope composition of groundwaters and surface waters from Willaura, compared to meteoric water line for Adelaide (solid line; IAEA/WMO, 2001) and open water evaporation line (dashed).

in winter, or shortly thereafter (spring), when rainfall exceeds evaporation, soils are saturated and hydraulic conductivities are greatest.

Groundwater in borehole 327 also plots on the MWL (Fig. 4), but is $\sim 1.5\text{‰}$ heavier ($\delta^{18}\text{O}$) than the other Willaura groundwaters. It is also deeper and much further along the regional flow path than the other groundwaters analysed for stable isotopes, and as might be expected, is the oldest groundwater dated during this study (~ 8000 years; Table 2). Many springs are discharging older groundwater and also have heavier $\delta^{18}\text{O}$ compositions (discussed further below). The climate of the study area ~ 8000 years BP, as indicated by palynological data from Lake Bolac, ~ 20 km southeast of Willaura, was warmer and wetter than at present (Crowley and Kershaw, 1994), consistent with similar palaeo-climate studies from south-eastern Australia (e.g. D'Costa et al., 1989; Wasson and Donnelly, 1991). Rainfall was subsequently more enriched at this time, as indicated by speleothems in western Tasmania (Goede and Hitchman, 1984), where rainfall patterns are similar to those of the study area. Thus, the isotopically heavier signature of the ~ 8000 year old groundwater may be linked to the atmospheric circulation at the time; variations in the stable isotope composition of groundwater frequently reflect climatic changes (e.g. Rozanski, 1985; Vaikmae et al., 2001).

The enriched $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signature of the ~ 8000 year old groundwaters at Willaura has not previously been observed in groundwaters in south-eastern Australia. This is possibly due to the shorter flow times at Willaura (~ 8000 years), as compared with

Table 2

Groundwater ages from tritium and ^{14}C ($\pm 1\sigma$ error) determinations, and $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data. ^{14}C ages are determined using half-life of 5730 years (Stuiver and Polach, 1977). ANSTO analysis codes are QZF368 to QZF370. Tritium age determinations are qualitatively determined using the method of Clark and Fritz (1997) and comparison with rainfall analysis from Adelaide (IAEA/WMO, 2001).

Sample name	Date	Tritium (TU)	PMC	$\delta^{13}\text{C}$ (‰)	Apparent age (years)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)
244	03-May-00					−4.7	−26.8
244	21-Dec-00	<0.3			> 50	−4.5	−28.0
244	04-Jun-01	<0.3			> 50	−4.2	−28.0
244	04-Jun-01		61.4	−14.05	4032	−4.2	−28.0
324	04-May-00					−6.4	−39.0
324	21-Dec-00	2.1			8–10	−5.4	−36.0
324	04-Jun-01					−5.0	−28.0
325	20-Dec-00	<0.3			> 50		
327	03-May-00					−3.4	−16.9
327	20-Dec-00	<0.3			> 50	−3.5	−15.0
327	04-Jun-01		38.06	−12.96	7986		
328	03-May-00					−5.2	−31.6
328	20-Dec-00					−4.2	−25.0
328	04-Jun-01					−4.2	−31.0
5019	03-May-00					−4.9	−30.2
5019	20-Dec-00					−5.6	−32.0
5019	04-Jun-01					−4.4	−28.0
5020	04-Jun-01					−4.9	−35.0
5201	04-Jun-01	0.56			> 50		
87755	04-Jun-01	<0.3			> 50		
Boggy Creek	03-May-00					−3.1	−14.3
Boggy Creek	21-Dec-00	0.6			30–35	−3.5	−16.0
Boggy Creek	04-Jun-01	4.0			<5	−2.9	−22.0
Gellerts Seep	03-May-00					−2.6	−11.5
Gellerts Seep	21-Dec-00	<0.3			> 50	−2.9	−19.0
Gellerts Seep	04-Jun-01		72.63	−9.67	2640	−3.7	−25.0
Johns Seep	04-May-00					−3.7	−18.4
Johns Seep	23-Dec-00	0.6			30–35	−3.0	−13.0
Johns Seep	04-Jun-01					−2.1	−17.0
Gellerts Lake	04-Jun-01					3.0	7.0
Gellerts Lake	21-Dec-00					−2.1	−7.0
Lake Muirhead	04-May-00					−3.5	−17.9

most other groundwater flow systems in south-eastern Australia subject to palaeoclimatic investigations (e.g. Love et al., 1994; Cartwright and Weaver, 2004).

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ composition of Willaura groundwaters for some bores show significant inter-annual variation over the sampling period (May 2000–June 2001), given that most recharge occurs consistently in winter and early spring. Borehole 324, on the slopes of the Grampians Ranges (Fig. 1), shows the largest difference (1.4‰ $\delta^{18}\text{O}$), because groundwater is recharged rapidly through the thin permeable soils so that the variability in rainfall isotopic composition (up to 14‰ $\delta^{18}\text{O}$ at Adelaide;

IAEA/WMO, 2001) is homogenised less than if the groundwaters were recharged slowly through low-permeability soils. Further down gradient the isotopic signatures show less than 1‰ $\delta^{18}\text{O}$ variability at individual sites, due to increasing residence times of diffuse recharge moving through the unsaturated zone, such that differences in rainfall isotopic composition are homogenised. Borehole 327 in the deepest, valley-filling part of the basalt shows no variation, expected given its depth and position down gradient (Fig. 1).

The lake waters and some spring samples at Willaura are strongly affected by evaporation, in

contrast to the groundwaters, which show no evaporative influence. The stable isotope compositions of the evaporated samples are displaced from the MWL along a line with a slope of 4.8 (Fig. 4), typical of evaporation at moderate humidity (Gonfiantini, 1986), such as at Willaura (mean 56% humidity; data from Bureau of Meteorology, Australia). The evaporation line intersects the MWL at the average winter rainfall composition, so the dominant source of these springs and lakes is modern precipitation, consistent with the tritium content of many spring samples (Table 2; see later discussion). The stable isotope compositions of the lake waters show a large amount of seasonal variation (up to 5‰ $\delta^{18}\text{O}$), due to increased evaporation over summer.

Those spring waters not affected by open water evaporation plot on the MWL (Fig. 4), but are heavier than most groundwaters, and cluster around the composition of bore 327. These springs (Boggy Creek, Gellerts Seep and Johns Seep) lie at the end of the groundwater flow path and feed the Cockajemmy Lakes, and are discharging old, isotopically heavy groundwaters (as described above for bore 327). Mixed with the older groundwater is modern rainfall and/or modern groundwaters, as shown by the tritium content of some spring waters (see below).

7. Groundwater dating

Of the 11 samples analysed for tritium to determine groundwater age, six have tritium counts below detection limit (0.3 TU; Table 2). This value is considered well below baseline for pre-1950s recharge at Adelaide (IAEA/WMO, 2001), indicating that the water at these sites has spent more than 50 years in the aquifer. Three of these older waters were subsequently dated using ^{14}C (see following discussion). Approximate ages have been derived for the five samples with >0.3 TU (Table 2), based on the tritium content of rainfall collected between 1962 and 1986 at Adelaide (IAEA/WMO, 2001).

The youngest groundwater is from the recharge area on the slopes of the Grampians Ranges (borehole 324, 8–10 years old; Table 2). Groundwaters increase in age rapidly away from the Grampians Ranges; 4 km down gradient in the same alluvial aquifer, groundwater from borehole 5201 has an age of 30–35

years (Table 2). Further down gradient, no tritiated borehole water is found in the deeper boreholes (>10 m), indicating ages greater than 50 years. The addition of diffuse saline recharge down gradient, infiltrating from the soil above and causing groundwaters to become progressively more saline, may add tritiated water to shallow groundwater in the basalt and alluvial aquifers, but there are no shallow boreholes down gradient to verify this. However, Boggy Creek spring in December 2000 contained 0.6 TU (Table 2), consistent with a mixture of modern tritiated basalt or alluvial groundwater and older non-tritiated Palaeozoic basement groundwater. In June 2001, Boggy Creek spring contained 4.0 TU, representing modern recharge with no addition of older groundwater, so spring flow at this time was dominated by recent rainfall (~260 mm in the three months preceding sampling; data from Bureau of Meteorology, 2004).

Two deep groundwater samples in the basalt and basement aquifers were dated using ^{14}C (boreholes 327 and 244, respectively; Table 2). Contamination by modern carbon is unlikely; the samples contain no detectable tritium (Table 2), and came from so deep in the aquifers that they were not affected by leakage of young water recharged down gradient. Any addition of dead carbon was probably minor; the basalt and basement aquifers contain little or no organic matter or calcite, and although the overlying alluvial aquifer does contain carbonaceous material, leakage into the deeper aquifers is minor, given the substantial differences in groundwater salinity between them.

Furthermore, it can be demonstrated that calcite dissolution is not contributing significant levels of dead carbon to the groundwater, because this process typically gives $\delta^{13}\text{C}$ groundwater signatures close to zero (Mook, 2001). The $\delta^{13}\text{C}$ composition of Willaura groundwaters is much lighter (–14.05 and –12.06‰; Table 2), consistent with C sourced from the decay of C_3 plants, which make up ~82% of all vegetation in south-western Victoria (Hattersley, 1983). Recharge waters beneath such vegetation typically have $\delta^{13}\text{C}$ values of ~14‰ at moderate pH (Clark and Fritz, 1997). The Willaura groundwater $\delta^{13}\text{C}$ values cannot be used for reservoir correction of the radiocarbon ages because the $\delta^{13}\text{C}$ composition of carbon from the alluvial aquifer is unknown.

The ^{14}C ages from boreholes 244 and 327 can be used to determine the approximate groundwater flow velocity, because any contamination by modern and/or dead carbon is probably minor, and in any case is likely to have affected each site equally, since waters in the Palaeozoic basement (244) laterally recharge the deeper segments of the basalt aquifer (327). The older sample (7986 years) is ~ 12 km further down gradient than the younger (4032 years; Table 1). This yields an approximate flow velocity of 3 km/1000 years, or $\sim 1 \times 10^{-7}$ m/s, a value typical of fractured rock aquifers (assuming 5% porosity; Domenico and Schwartz, 1998). Therefore on average, groundwater takes around 8000 years to flow from the recharge areas in the Grampians Ranges to discharge springs at the Cockajemmy Lakes (average 25 km flow length through the Palaeozoic basement and alluvial aquifers). There are zones of variable fracture density, and therefore, hydraulic conductivity within the basement aquifer, so flow velocities may vary substantially around the calculated value. This probably explains why the groundwater ^{14}C ages for boreholes 244 and 327 are older than would be expected from the calculated flow velocity.

A spring (Gellerts Seep; Fig. 1) was also dated by ^{14}C , and gave an age of 2640 years (Table 2). This water represents discharge at the end of the flow path, and should therefore be at least 8000 years old. As with Boggy Creek spring (see above), modern meteoric water is mixing with older Palaeozoic basement groundwater at Gellerts Seep, adding modern carbon and decreasing the apparent age of the sample.

The ^{14}C groundwater ages show clearly that the progressive down gradient salinisation of Willaura groundwater, due to cumulative additions of saline soil–water, has taken place over thousands of years and is therefore natural (primary) groundwater salinity.

8. Conclusions

The Willaura catchment, which is strongly affected by salinisation, shows prominent down gradient changes in the hydrochemical and isotopic compositions of groundwaters, and these have been used to formulate a model for the development of primary salinity. Groundwaters in the main recharge area on

the slopes of the Grampians Ranges are fresh and young, containing tritium, show significant interannual variations in stable isotope composition, and infiltrated rapidly through thin, sandy soils. The stable isotope compositions show that the majority of recharge occurs in winter or spring. Down gradient groundwaters are recharged through thick clay soils. Infiltration is slow, so any differences in the isotopic composition of rainfall are homogenised, and the recharge water in the clay soils is strongly concentrated by evapotranspiration. When progressively added to the underlying fresher groundwater, the infiltrating soil water causes the groundwater to gradually increase in salinity down gradient. Carbon-14 dating indicates that it takes ~ 8000 years for groundwater to flow from recharge areas in the Grampians Ranges to discharge areas at the Cockajemmy Lakes. Thus the increase in salinity down gradient is natural and has occurred across the area throughout the Holocene. This model (in combination with secondary processes like evaporation) probably applies to other catchments in Australia that demonstrate similar down gradient primary salinisation.

Water–rock interaction processes cause a reduction in the overall groundwater salinity down gradient, due to removal of ions by conversion of kaolinite to smectite and illite, and cation exchange of Na^+ for Ca^{2+} on smectite. These reactions increase pH and decrease many species/ Cl^- ratios down gradient. Silicate weathering and sulphide and organic matter oxidation processes are also evident, the latter causing a decline in redox potential down gradient.

Acknowledgements

The authors would like to thank Dr Ian Cartwright of Monash University for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analysis, Dr Fuping Hao of CSIRO Division of Minerals for use of HPLC, and John and Lynn Anderson for providing accommodation and meals whilst in the field. Discussions and comments from Dr Dirk Kirste, Mr Matthew Edwards, Dr Gideon Tredoux and an anonymous reviewer helped to improve the manuscript. Willaura Landcare, the Centre for Land Protection Research, DPI, Bendigo and AINSE Grant 01/1855 funded this work.

References

- Allison, G.B., Barnes, C.J., Hughes, M.W., Leaney, F.W., (1984). Effect of climate and vegetation on oxygen-18 and deuterium profiles in soils, *Isotope Hydrology 1983*, IAEA Symposium 270, Vienna, pp. 105–123.
- Arad, A., Evans, R., 1987. The hydrogeology, hydrochemistry and environmental isotopes of the Campaspe River aquifer system, north-central Victoria, Australia. *Journal of Hydrology* 95 (1–2), 63–86.
- Bennetts, D.A., Webb, J.A., (2004). Processes affecting groundwater quality in a basalt aquifer system in southern Australia. In: R.B. Wanty and R.R. Seal (Editors), *Proceedings - International Symposium on Water-Rock Interaction 11*. Balkema, Rotterdam, pp. 347–351.
- Blackburn, G., Mcleod, S., 1983. Salinity of atmospheric precipitation in the Murray-Darling drainage division, Australia. *Australian Journal of Soil Research* 21, 411–434.
- Blake, R., (1989). The origin of high sodium bicarbonate waters in the Otway Basin, Victoria, Australia. In: D.L. Miles (Editor), *Proceedings - International Symposium on Water-Rock Interaction 6*. Balkema, Rotterdam, pp. 83–85.
- Bormann, M., (2004). Temporal And Spatial Trends In Rainwater Chemistry Across Central And Western Victoria. Honours Thesis, La Trobe University.
- Buckland, G.L., 1986. Geology and mineral potential of the Mount Stavely Volcanic Complex. Geological Survey of Victoria Report, 80.
- Bureau of Meteorology, (2004). Bureau of Meteorology climate data available at <http://www.bom.gov.au/>.
- Camilleri, M.A., (1999). Regolith of the Mt Stavely area, western Victoria: northwest part of the Willaura 1:100,000 mapsheet. Honours Thesis, La Trobe University.
- Cartwright, I., Weaver, T., 2004. Hydrogeochemistry of the Goulburn Valley region of the Murray Basin, Australia: implications for flow paths and resource vulnerability. *Hydrogeology Journal*.
- Cartwright, I., Weaver, T.R., Fulton, S., Nichol, C., Reid, M.C., X., (2004). Hydrogeochemical and isotopic constraints on the origins of dryland salinity, Murray Basin, Victoria, Australia. *Applied Geochemistry*, 19(8): 1233–1254.
- Cayley, R.A., Taylor, D.H., 1997. Grampians special map area geological report. Geological Survey of Victoria Report, 107.
- Clark, I., Fritz, P., 1997. *Environmental Isotopes in Hydrogeology*. Lewis Publishers, New York, NY.
- Crowley, G.M., Kershaw, A.P., 1994. Late Quaternary environmental change and human impact around Lake Bolac, western Victoria, Australia. *Journal of Quaternary Science* 9 (4), 367–377.
- Davis, S.N., Whittemore, D.O., Fabryka-Martin, J., 1998. Uses of chloride/bromide ratios in studies of potable water. *Ground Water* 36 (2), 338–350.
- D'Costa, D.M., Edney, P.A., Kershaw, A.P., De Deckker, P., 1989. Late Quaternary palaeoecology of Tower Hill, Victoria, Australia. *Journal of Biogeography* 16, 461–482.
- De Deckker, P., (2003). Saline playa-groundwater in the Western District of Victoria. In: I.C. Roach (Editor), *Advances in Regolith*. CRC LEME, pp. 91–94.
- Dogramaci, S.S., Herczeg, A.L., Bone, Y., (1998). Chemical evolution of groundwater in the Murray Basin; geochemistry and mass transfer modelling, 1st Australian Geological Convention. Geological Society of Australia Abstracts, pp. 115.
- Domenico, P.A., Schwartz, F.W., 1998. *Physical and Chemical Hydrogeology*. Wiley, New York, NY.
- Drever, J.I., (1997). *The geochemistry of natural waters: surface and groundwater environments*. Prentice Hall, Upper Saddle River, N.J.
- Edmunds, W.M., Guendouz, A.H., Mamou, A., Moulla, A., Shand, P., Zouari, K., 2003. Groundwater evolution in the Continental Intercalaire Aquifer of southern Algeria and Tunisia; trace element and isotopic indicators. *Applied Geochemistry* 18 (6), 805–822.
- Elliot, T., Andrews, J.N., Edmunds, W.M., 1999. Hydrochemical trends, palaeorecharge and groundwater ages in the fissured Chalk aquifer of the London and Berkshire Basins, UK. *Applied Geochemistry* 14 (3), 333–363.
- Ghassemi, F., Jakeman, A.J., Nix, H.A., 1995. *Salinisation of Land and water Resources; Human causes, Extent, Management and Case studies*. University of New South Wales Press, Sydney, Australia.
- Glenn Hopkins Regional Catchment Strategy, (2003). Glenn Hopkins Catchment Management Authority, Hamilton, Victoria.
- Goede, A., Hitchman, M.A., (1984). Late Quaternary climatic change; evidence from a Tasmanian speleothem. In: J.C. Vogel (Editor), *Late Cainozoic palaeoclimates of the Southern Hemisphere*. Balkema, Rotterdam, pp. 221–232.
- Hattersley, P.W., 1983. The distribution of C3 and C4 grasses in Australia in relation to climate. *Oecologia* 57, 113–128.
- Herczeg, A.L., Torgersen, T., Chivas, A.R., Habermehl, M.A., 1991. Geochemistry of ground waters from the Great Artesian Basin, Australia. *Journal of Hydrology* 126 (3–4), 225–245.
- Herczeg, A.L., Dogramaci, S.S., Leaney, F.W., 2001. Origin of dissolved salts in a large, semi-arid groundwater system: Murray Basin, Australia. *Marine and Freshwater Research* 52, 41–52.
- Hills, E.S., (1975). *Physiography of Victoria: an introduction to geomorphology*. Whitcombe & Tombs, Marrickville, N.S.W.
- Hutton, J.T., Leslie, T.I., 1958. Accession of non-nitrogenous ions dissolved in rainwater to soils in Victoria. *Australian Journal of Agricultural Research* 9, 59–84.
- IAEA/WMO, (2001). *Global Network for Isotopes in Precipitation*. The GNIP Database accessible at <http://isohis.iaea.org>.
- Jankowski, J., Acworth, I., 1993. The hydrogeochemistry of groundwater in fractured bedrock aquifers beneath dryland salinity occurrences at Yass, NSW. *AGSO Journal of Australian Geology and Geophysics* 14 (2), 279–285.
- Jenkin, J.J., Dyson, P.R., (1983). Groundwater and soil salinisation near Bendigo, Victoria. In: M.J. Knight, E.J. Minty, R.B. Smith (Editors), *Collected case studies in engineering geology, hydrogeology and environmental geology*. Geological Society of Australia, Sydney, Australia, pp. 229–257.
- Jones, B.F., Hanor, J.S., Evans, W.R., 1994. Sources of dissolved salts in the central Murray Basin. *Australia Chemical Geology* 111 (1–4), 135–154.
- Joplin, G.A., (1963). *Chemical analyses of Australian rocks; part I, Igneous and metamorphic*. Bureau of Mineral Resources, Geology and Geophysics Bulletin, 65, Canberra.
- Komarower, P.J., Wall, V.J., (1979). The chemical evolution of the groundwaters in the Tertiary basalts of Victoria. In: C.R. Lawrence, R.J. Hughes (Editors), *Proceedings of the Groundwater Pollution Conference*, Perth, W.A., pp. 290–307.

- Lawson, E.M., Elliot, G., Fallon, J., Fink, D., Hotchkis, M.A.C., Hua, Q., Jacobsen, G.E., Lee, P., Smith, A.M., Tuniz, C., Zoppi, U., 2000. AMS at ANTARES - The First 10 years. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 172, 95–99.
- Leaney, F.W., Herczeg, A.L., Walker, G.R., 2003. Salinization of a fresh palaeo-ground water resource by enhanced recharge. *Ground Water* 41 (1), 84–92.
- Love, A.J., Herczeg, A.L., Leaney, F.W., Stadter, M.F., Dighton, J.C., Armstrong, D., 1994. Groundwater residence time and palaeohydrology in the Otway Basin, South Australia: 2H, 18O and 14C data. *Journal of Hydrology* 153 (1–4), 157–187.
- Macumber, P.G., (1991). Interaction between groundwater and surface systems in northern Victoria. Department of Conservation and Environment, Victoria.
- Macumber, P.G., 1992. Hydrological processes in the Tyrrell Basin, south-eastern Australia. In: W.B. Lyons, D.T. Long, A.L. Herczeg and M.E. Hines (Editors), *The geochemistry of acid groundwater systems*, Chemical Geology, 1992, pp. 1–18.
- Mann, B.S., Nolan, J., 1989. Preliminary hydrogeological appraisal of the Willaura west region. Rural Water Commission Report, 1989/37.
- Mann, B.S., Stanley, D.R., Bolger, P.F. Basalt plains hydrogeological salinity investigation, Progress Report no. 2 (1992) 1992/1
- Mazor, E., George, R., 1992. Marine airborne salts applied to trace evapotranspiration, local recharge and lateral groundwater flow in Western Australia. *Journal of Hydrology* 139, 63–77.
- McArthur, J.M., Turner, J., Lyons, W.B., Thirlwall, M.F., 1989. Salt sources and water-rock interaction on the Yilgarn Block, Australia; isotopic and major element tracers. *Applied Geochemistry* 4 (1), 79–92.
- Mitchell, T.L., (1839). Three expeditions into the interior of Eastern Australia: with description of the recently explored region of Australia Felix, and of the present colony of New South Wales. T. & W. Boone, London.
- Mook, W.G., (2001). Environmental Isotopes in the Hydrological Cycle: Principles and Applications. UNESCO/IAEA. Available online at <http://www.iaea.or.at/programmes/ripc/ih/volumes/volumes.htm>.
- National Land and Water Resources Audit, (2001). Australian Dryland Salinity Assessment 2000: Extent, Impacts, Processes, Monitoring and Management Options, Land and Water Australia, Canberra.
- Price, R., (1994). The occurrence of saline pools in the non-estuarine section of the Hopkins River. Department of Conservation and Natural Resources, South West Area, Melbourne.
- Rosen, M.R., Coshell, L., Turner, J.V., Woodbury, R.J., 1996. Hydrochemistry and nutrient cycling in Yalgorup National Park, Western Australia. *Journal of Hydrology* 185 (1–4), 241–274.
- Rozanski, K., 1985. Deuterium and oxygen-18 in European groundwaters; links to atmospheric circulation in the past. *Chemical Geology* 52 (3–4), 349–363.
- Salama, R.B., Farrington, P., Bartle, G.A., Watson, G.D., 1993a. The chemical evolution of groundwater in a first-order catchment and the process of salt accumulation in the soil profile. *Journal of Hydrology* 143 (3–4), 233–258.
- Salama, R.B., Wells, A.S.M., Farrington, P., Bartle, G.A., (1993b). The chemical evolution of groundwater in the aquifer system of the Yilgarn Craton of western Australia. CSIRO Division of Water Resources Report, Perth.
- Salama, R.B., Otto, C.J., Fitzpatrick, R.W., 1999. Contributions of groundwater conditions to soil and water salinization. *Hydrogeology Journal* 7, 46–64.
- Schofield, S., Jankowski, J., 2003. The hydrogeology of the Ballimore region, central New South Wales, Australia; an integrated study. *Environmental Geology* 44 (1), 90–100.
- Sibley, G.T., (1967). A study of the land in the Grampians area. Soil Conservation Authority, Melbourne.
- Simmons, C.T., Narayan, K.A., 1998. Modelling density-dependent flow and solute transport at the Lake Tutchewop saline disposal complex, Victoria. *Journal of Hydrology* 206 (3–4), 219–236.
- Smith, W.E., Nathan, R.J., (1999). Victorian water quality monitoring network trend analysis: Glenelg Catchment Management Authority area, Sinclair Knight Mertz Report.
- Stanley, D.R., (1983). Final report on phase 1 exploration for drilling project GC13: lignite potential of the northern margin of the Otway Basin. 1983/69, Geological Survey of Victoria Report.
- Street, G.J., Pracillo, G., Nallan Chakravartula, P., Nash, C., Harvey, B., Sattel, D., Owers, M., Triggs, D., Lane, R., (1998). Willaura saltmap survey - Interpretation report. World Geoscience Corporation Limited.
- Stuart-Smith, P.G., Black, L.P., (1999). Willaura sheet 7422, Victoria, 1:100,000 map geological report. 1999/38, Australian Geological Survey Organisation Report.
- Stuiver, M., Polach, H.A., 1977. Discussion; reporting of C-14 data. *Radiocarbon* 19 (3), 355–363.
- Swane, I.P., Weaver, T.R., Cartwright, I., Lawrence, C.R., (2001). Hydrologic controls on groundwater salinisation, Murray Basin, Australia. In: R. Cidu (Editor), *Tenth International Symposium on Water-Rock Interaction*. Balkema, Rotterdam, Villasilimus, Italy, pp. 589–592.
- Turner, J.V., Arad, A., Johnston, C.D., 1987. Environmental isotope hydrology of salinized experimental catchments. *Journal of Hydrology* 94, 89–107.
- Vaikmae, R., Vallner, L., Loosli, H.H., Blaser, P.C., Juillard-Tardent, M., 2001. Palaeogroundwater of glacial origin in the Cambrian-Vendian aquifer of northern Estonia. *Geological Society Special Publications* 189, 17–27.
- VandenBerg, A.H.M., Willman, C.E., Maher, S., Simons, B.A., Cayley, R.A., Taylor, D.H., Morand, V.J., Moore, D.H., Radokovic, A., (2000). The Tasman Fold Belt System in Victoria. Geological Survey of Victoria Special Publication.
- Vaught, T.L. Temperature gradients in a portion of Michigan: a review of the usefulness of data from AAA geothermal survey of North America, Department of Energy Report, (1980) DOE/NV/10072–DOE/NV/10071
- Wasson, R.J., Donnelly, T.H., (1991). Palaeoclimatic reconstructions for the last 30,000 years in Australia - A contribution to prediction of future climate. 91/3, CSIRO Division of Water Resources Technical Paper.
- Williams, B., (1997). A preliminary analysis of groundwater records, Willaura region, Victoria, Unpubl. Report.