Assessing catchment-scale spatial and temporal patterns of groundwater and stream salinity

David L. Poulsen · Craig T. Simmons · Corinne Le Galle La Salle · Jim W. Cox

Abstract Understanding catchment-scale patterns of groundwater and stream salinity are important in landand water-salinity management. A large-scale assessment of groundwater and stream data was undertaken in the eastern Mt Lofty Ranges of South Australia using geographical information systems (GIS), regional scale hydrologic data, hydrograph separation and hydrochemical techniques. Results of the study show: (1) salts were mostly of marine origin (75%), while sulfate and bicarbonate from mineral weathering comprised most of the remainder, (2) elevated groundwater salinities and stable water isotopic compositions similar to mean rainfall indicated that plant transpiration was the primary salt accumulation mechanism, (3) key factors explaining groundwater salinity were geology and rainfall, with overall catchment salinity inversely proportional to average annual rainfall, and groundwater salinity 'hotspots' (EC >8 mS/cm) associated with geological formations comprising sulfidic marine siltstones and shales, (4) shallow groundwater correlated with elevated stream salinity, implying that baseflow contributed to stream salt loads, with most of the annual salt load (estimated to be 24,500 tonnes) occurring in winter when baseflow volume was highest. Salt-load analysis using stream data could be a practical, low-cost technique to rapidly target the investigation of problem areas within a catchment.

Résumé Comprendre les mécanismes de la salinité des nappes et des rivières, à l'échelle des bassins-versants, est important pour la gestion de la salinité des sols et de l'eau. Une étude à grande échelle de l'eau souterraine et des cours d'eau a été menée dans la partie Est des Mount Lofty Ranges dans le Sud de l'Australie, au moyen d'un

Received: 15 December 2004/Accepted: 19 May 2006 Published online: 24 August 2006

© Springer-Verlag 2006

D. L. Poulsen · C. T. Simmons (⊠) · C. Galle La Salle School of Chemistry, Physics and Earth Sciences, Flinders University, GPO Box 2100, Adelaide, SA 5001, Australia e-mail: craig.simmons@flinders.edu.au

J. W. Cox CSIRO Land and Water and CRC LEME, PMB 2, Glen Osmond, SA 5064, Australia

Hydrogeology Journal (2006) 14: 1339-1359

système d'information géographique (SIG), des données hydrologiques régionales, la séparation des hydrographes et des techniques hydrochimiques. Les résultats de l'étude montrent : (i) que les sels sont essentiellement d'origine marine (75%), tandis que les sulfates et les bicarbonates provenant de l'altération minérale comprendraient surtout les « soldes », (ii) la salinité élevée dans les eaux souterraines et la composition isotopique stable similaire à celle des eaux de pluie, indiquent que la transpiration des plantes fut le mécanisme primaire de l'accumulation du sel, (iii) les facteurs clés expliquant la salinité de l'eau souterraine où la géologie et l'eau de pluie, et une salinité globale inversement proportionnelle à la pluie moyenne annuelle, des spots de salinité (Conductivité > 8 mS/cm) associés à des formations géologiques comprenant des silts compacts et des shales marins et sulfurés, (iv) les nappes phréatiques corrélées avec une salinité des cours d'eau élevée, impliquant de fait la contribution des écoulements de base à la charge en sel des cours d'eau, avec une charge maximum annuelle en hiver (estimée à 24 500 tonnes) lorsque l'écoulement de base devient plus important. L'analyse des charges en sel utilisant les données des rivières pourrait s'avérer être une technique pratique et peu coûteuse pour rapidement pointé la bonne investigation à entreprendre dans les zones à problèmes d'un bassin-versant.

Resumen El conocimiento a escala de cuenca de los patrones de salinidad de agua fluvial y subterránea son importantes para la gestión de la salinidad del agua y suelo. Se ha llevado a cabo una evaluación en gran escala de datos de agua de río y agua subterránea en las cordilleras del Monte Lofty del sur de Australia utilizando un Sistema de Información Geográfico (SIG), datos hidrológicos de escala regional, y técnicas hidroquímicas y de separación de hidrogramas. Los resultados del estudio son los siguientes: (1) el 75% de las sales son de origen marino mientras que el restante 25% comprenden sulfato y bicarbonato derivados de intemperismo mineral, (2) las elevadas salinidades del agua subterránea y las composiciones de isótopos estables similares a la composición media de la lluvia indican que el principal mecanismo primario de acumulación de sal es la transpiración de las plantas, (3) los factores clave que explican la salinidad del agua subterránea son geología y lluvia, con una salinidad promedio para la cuenca en proporción

1340

inversa al promedio anual de lluvia, y puntos anómalos de salinidad de agua subterránea (CE >8 mS/cm) asociados con formaciones geológicas compuestas de lutitas y lodolitas marinas sulfurosas, (4) agua subterránea somera correlacionada con salinidad elevada en agua de río, lo que implica que el flujo de base contribuye cargas saladas al río, con gran parte de la carga salada anual (estimada en 24,500 tons) ocurriendo en invierno cuando el volumen de flujo base es más elevado. Los análisis de la carga salada en base a datos de río puede ser una técnica práctica y de bajo costo para orientar rápidamente la investigación de áreas problemáticas dentro de una cuenca.

Keywords Salinization · Salt-water/fresh-water relations · GIS · Bremer River catchment · Groundwater flow

Introduction

Stream salinization from groundwater discharge is one of the largest offsite impacts of dryland salinity. Large salt export in streamflow from catchments of the eastern Mt Lofty Ranges, South Australia (Fig. 1) has been identified as a significant problem for downstream water users and



Fig. 1 Location of a the eastern Mt Lofty Ranges, South Australia, b the Bremer River catchment study area and other research catchments and c sampling sites within the study area (catchments of the Upper and Lower Bremer Rivers, Mt Barker Creek and Rodwell/Red Creeks). m AHD = metres at Australian Head Datum (or metres above mean sea level: m amsl)

aquatic ecosystems. Like most areas in Australia, salt mobilization in the Mt Lofty Ranges has occurred in response to clearance of native vegetation for agriculture and increased saline groundwater discharges to streams resulting from elevated water tables. Reducing the extent of near-surface saline groundwater requires specific knowledge of the location of catchment salt stores, areas of shallow groundwater and the temporal patterns of groundwater and salt discharge to streams.

It is now well established that native vegetation removal has caused increased groundwater recharge and mobilization and transport of stored salts (Peck and Hurle 1973; Williamson et al. 1987), particularly in areas where there is high natural salt storage in the unsaturated zone. Salinity is a diffuse contaminant but may also be sourced from local 'hotspots' in the landscape, both of which contribute to salt export from a catchment. This study characterizes the net salt export by integrating the spatial and temporal patterns of salinity throughout a river catchment. Salt export from cleared catchments is usually well in excess of salt input and is primarily sourced from groundwater discharge to streams (e.g. Williamson et al. 1987). Salt output/input ratios across most of the study catchment have been estimated previously at between 5.5 and 7.6 (Williamson and van der Wel 1991) and as high as 15.1 (Ecker 1998). These rates of salt export are considerably higher than for other lower Murray Basin catchments, for which salt output/input ratios commonly range between 1.2 and 2.5 (Jolly et al. 2001). The rate of salt export from a catchment is governed by rainfall, hydrogeological conditions, salt storage, catchment size and amount of vegetation clearance (Jolly et al. 2001). For catchments where rainfall was between 490–1,120 mm/year, Peck and Hurle (1973) estimated the time required to reach salt equilibrium following clearing to be in the range 30-400 years. Catchments situated in low rainfall zones typically have high stream salinity and salt storage, while those in high rainfall zones more rapidly export stored salts and thus have low salt storage and stream salinity (Schofield and Ruprecht 1989). Although stream salinity in the eastern Mt Lofty Ranges is generally high, Jolly et al. (2000) showed that over the last 20–30 years, salinity trends are either statistically not significant or are decreasing. Further, they noted that the final phase of vegetation clearing was completed more than 50 years ago and suggested that the peak of salt export may have been reached or already passed.

It is thought that sodium and chloride-dominated salts existing naturally in the Australian landscape are mostly sourced from atmospheric deposition of marine and continentally derived aerosols that have accumulated in the soil over many thousands of years (Herczeg et al. 2001). Prior to clearing of native vegetation, a large storage of salts in the landscape developed by a continual cycle of water and solute input as rainfall and solute concentration in the subsurface by partial evaporation and plant transpiration of water. However, since clearing, higher groundwater recharge by rainfall and subsequent elevated water tables have mobilized these stored marine

salts and they are being transported by large water fluxes through catchments. Secondary weathering of rock minerals has also been cited as a source of salt in some areas, including the Mt Lofty Ranges, where weathering of saprolites and sulfidic minerals may be contributing to locally elevated groundwater salinity (Fitzpatrick et al. 1996).

A key feature of successful dryland salinity management is an approach that targets amelioration strategies at specific areas within a catchment such as salt generation zones and transport pathways (Cox et al. 2002b). However, the effective application of a targeted approach requires detailed knowledge of catchment hydrology, salt stores and salt transport processes. In the Mt Lofty Ranges, land degradation processes have been documented at the subcatchment scale (~2 km²), including salinization (Fitzpatrick et al. 1996) and waterlogging (e.g. Cox et al. 1996), most notably in the Herrmanns and Keynes subcatchments (Fig. 1). Although the processes of salinization are now well understood, the locations, causes and consequences of salt-load 'hotspots' at the broad catchment scale have yet to be identified in detail. To meet this objective, a regional study is under way, covering a large portion (hundreds of square kilometres) of the eastern Mt Lofty Ranges including a portion of the Bremer River catchment and catchments draining into the Murray River to the north (Cox et al. 2002a). In parallel with that study, the work presented here is a key step in developing a regional salinity management framework.

In this study, the sources and spatiotemporal patterns of salinity and stream salt loads in the upland catchments of the Bremer River system (Fig. 1), in the eastern Mt Lofty Ranges, are investigated. The large amount of existing hydrological and hydrochemical data, collected over the last 50 or more years by many different organizations, were systematically compiled and assessed using an integrated suite of tools including a geographical information system (GIS) and hydrograph separation (HYDSYS) software in addition to standard numerical procedures. Previous studies have assessed individual components of the data, including the analysis of stream salinity trends of Jolly et al. (2000) and the groundwater modelling and salt-balance analysis of Ecker (1998). However, this study represents the first systematic assessment of all available data at the catchment scale. The holistic research approach adopted in this study specifically enabled the identification of (1) the origin of salts, in particular the relative contributions of marine salts and mineral weathering, (2) factors influencing the distribution of groundwater salinity, (3) the spatial and temporal dynamics of stream salinity and salt loads and (4) the effect of temporal data resolution on interpretation of these dynamics.

This study clearly demonstrates the usefulness of employing regional scale databases in hydrogeologic analyses. In particular, the behaviour of salt export from catchments downstream is a spatiotemporal integration of salt loads across multiple upstream subcatchments. Saltload analysis using stream flow and salinity data at the subcatchment scale could be a practical, low-cost technique to rapidly target salinity investigations at problem areas within a catchment. This makes a regional scale approach a necessary requirement for assessing catchment salt loads and solute transport dynamics.

Study area

Regional setting

The Bremer River catchment, extending southeast from the central divide of the Mt Lofty Ranges to Lake Alexandrina, was selected as representative catchment of the drier more salt-affected eastern side of the Mt Lofty Ranges (eastern ranges). Existing data and a significant climatic gradient across the region made this catchment well suited to the integrated whole catchment approach used in this study and enabled direct comparison of salinization in two climatically different subcatchments. However, data were sparse in some areas of the catchment.

The Bremer River system drains approximately 810 km² of the lower western Murray Basin, flowing southeast out of the hills through the Langhorne Creek viticultural region before discharging into Lake Alexandrina. The study area, covering approximately 520 km² of hilly terrain in the eastern Mt Lofty Ranges (Fig. 1), was defined by the Mt Barker Creeks (MBC), Upper Bremer River (UBR) and Rodwell/Red Creeks (RRC) subcatchments in the upland portion of the Bremer River system. The inclusion of the RRC subcatchment in this study was limited by a lack of existing instrumentation or sampling in that area.

Land clearing in this region occurred in two main phases, the first between 1860 and 1880 and the second between 1930 and 1950, and the current native remnants are primarily roadside vegetation. Currently the main land uses are cropping, grazing and, more recently, viticulture due to the thriving wine industry.

The climate grades from temperate in the west to semiarid in the east. In the west, orographic rain falls for about 8 months of the year mostly between May and October, resulting in an overall wetter climate. Average annual rainfall across the Bremer River catchment decreases along a strong gradient to the east by approximately 15-30 mm/km between Mt Barker and Callington (Fig. 2). At Mt Barker (360 m AHD = metres at Australian Head Datum or m amsl) the climate is temperate, with a 100year mean annual rainfall and potential evaporation of 762 and 1,291 mm/year respectively and rainfall exceeds evaporation from May to September. While at Callington (86 m AHD) the climate is semi-arid, with a 100-year mean annual rainfall and potential evaporation of 378 and 1,549 mm/year respectively and monthly rainfall never exceeds potential evaporation.

Dissolved salts in rainfall are sodium and chloride dominant because they originate as marine aerosols. Concentrations decrease with distance inland from the Adelaide coastline, and in the Mt Lofty Ranges rainfall has been found to contain around 13.5 mg/L total dissolved solids (TDS; Blackburn and McCleod 1983). A time-averaged chemical composition of rainfall at a single sampling station at Verdun, located 12 km northwest of Mt Barker and outside of the study area, is provided in Fig. 2.

Geology and hydrogeology

The rocks of the Mt Lofty Ranges, from oldest to youngest, are Proterozoic, Cambrian and Tertiary in age. The hydrogeology of the Bremer River catchment is defined by the Pre-Cambrian aged Adelaidean formations, the metasedimentary formations of the Cambrian aged Kanmantoo Group, and the overlying Tertiary and Recent reworked alluvial sediments (Fig. 3). The Adelaidean rocks are feldspathic sandstones, siltstones, guartzites and dolomites, while the Kanmantoo metasediments are a complex sequence of marine sandstones, siltstones and shales. Limestone formations also occur in some localized areas. Within the Kanmantoo Group metasediments less common lithological units include pyritic shales, which occur as narrow discontinuous interbeds. Black carbonaceous and sulfidic deposits have been found to occur throughout the metasediments and have been associated with the development of saline sulfidic soils and groundwaters (Fitzpatrick et al. 1996).

Shale is composed primarily of soft clay minerals but may include variable amounts of organic matter, calcareous material and quartz grains. Numerous secondary minerals are associated with shales, including melanterite (hydrated iron sulfate) and copiapite (hydrated iron magnesium sulfate hydroxide). These water-soluble sulfate minerals are formed from the oxidation of iron sulfides (such as pyrite) by water moving through the landscape, and can contribute to weathering-derived dissolved salts in groundwater.

Both the Proterozoic and Cambrian sediments underwent uplifting and deformation along steeply-dipping reverse faults, and subsequent erosion during the Cenozoic has resulted in deposition of sediments in local basins and valleys. Denudation of the highlands continues to the present day with active stream incision and deposition on river floodplains and colluvial foot slopes. Tertiary and Recent sediments occur extensively as unconfined regolith and alluvial aquifers of up to 100 m in thickness.

The partial preservation of a palaeosurface and associated deep ferruginous weathering profiles is a feature of the Mt Lofty Ranges. The palaeosurface appears as scattered, typically ferruginous landscapes of relatively low relief. It is depicted as "Tertiary laterite" and is superimposed across a variety of different rock types and structures (Milnes et al. 1987). Bedrock and, in places, alluvial/colluvial sediments spatially associated with the palaeosurface are typically very highly weathered, with most of the primary minerals altered to clay.

Due to greater metamorphism of the Kanmantoo Group formations, their function as aquifers is considerably less



Fig. 2 Interpolated average annual rainfall across the Bremer River catchment. Note the gradient of decreasing rainfall to the east. Also shown is a time-averaged chemical analysis of rainfall at a single sampling station at Verdun (not shown on map), 12 km north-west of Mt Barker just outside the study area measured over the period 1974–1975 (Blackburn and McLeod 1983)

the overlying Tertiary and Recent sediments. In general to 1 m/day), whereas the Tertiary and Recent sediments the metasedimentary rocks will have hydraulic conductiv-

than some of the Adelaidean formations to the west and ities in the order of less than a few metres per day (0.0001 will have values of tens of metres per day (10–100 m/day).



Fig. 3 Surficial geology of the Bremer River Catchment, showing an interpreted association with groundwater salinity 'hotspots' (EC >8 mS/cm)

Although localized limestone units provide groundwater with low salt content, most Kanmantoo Group aquifers range in salinity between 3,000 and 10,000 mg/L TDS (Henschke 1997).

Soils and hydrology

Soils are characterized by sandy or loamy topsoils and clay-rich subsoils and are commonly referred to as duplex

soils. Duplex soils occupy about 80% of the Mt Lofty Ranges and can vary in depth from about 0.2 m on eroded hilltops to 1.8 m on foot slopes. These soils are associated with seasonal perched water tables and near-surface lateral flow, which converge with the local groundwater flow systems in topographic depressions and cause waterlogging and discharge to streams (Cox et al. 1996). Salt progresses through the landscape along the same flow paths as water, moving away from upland recharge areas and accumulating in valley discharge zones where evaporative concentration is active (Cox et al. 1999), and high stream solute loads have been observed (Cox and Ashley 2000).

Methods

Data sets

This study represents a compilation and analysis of all available existing groundwater and stream hydrological and hydrochemical data from across the Bremer River catchment. Collected over varying periods during the last 50 years, the data range from very large 20-year daily streamflow and salinity records to point measurements in both space and time of salinity and groundwater levels. The daily streamflow and salinity data sets have some gaps in the periods of record, with the flow data being more complete. The data were sourced from various different organizations all of whom are appropriately acknowledged.

The spatial density of groundwater and stream data across the catchment was low. In order to achieve sufficient spatial coverage of groundwater level and salinity and stream salinity, data recorded during the last 10–12 years were combined. Where time-series data existed for a sampling point, the mean value was calculated and used in the spatial data set. The combination of mean values with single values and measurements from different points in time was a limitation due to the presence of seasonal and long-term variations. However, given the limited size of the whole data set, there was greater value in combining all the data than considering much smaller subsets separately. Interpretations are thus a qualitative indication of the relative spatial distribution of the parameters.

Daily streamflow and salinity data were obtained from monitoring stations on the Bremer River and its tributaries as shown in Fig. 1. Flow data were only available for three sampling stations, two in the Mt Barker Creeks catchment on the Dawesley Creek (AW426558) and Mt Barker Creek downstream of Mt Barker (AW426557), and one further downstream on the Bremer River (AW426533) in the Lower Bremer catchment. Hydrochemical data were only available from the sampling station in the lower catchment (AW426533) and this provided an integration of all the upland subcatchments. No flow data were available for the Bremer River in the Upper Bremer catchment. The completeness of the data sets was determined by calculating the proportion of the total number of days within the duration of sampling for which measurements were recorded. The Dawesley Creek and Mt Barker Creek data sets covered the period from 1979–2002 and were 100 and 98% complete respectively, while the Bremer River data set extended from 1973-2002 and was 99% complete. Salinity data were obtained for three sampling stations, located one each on the Mt Barker Creek (AW426679) and Bremer River (AW426688), at the draining points of the Mt Barker

Creeks and Upper Bremer catchments, and the other on the Bremer River near Hartley (AW426533) in the Lower Bremer catchment. The station in the Lower Bremer catchment was the only one with records for both streamflow and salinity. The data sets for the Mt Barker Creek and Bremer River upstream of the confluence of the Mt Barker Creek and Upper Bremer River cover 6 years from 1997–2002 and were 68 and 72% complete respectively, while the data set for the station on the lower Bremer River covers 28 years from 1973–2002 and was 63% complete.

The total annual export of salt from the catchment was calculated using the daily streamflow and salinity datasets. In addition, this high temporal resolution data allowed the identification of time response dynamics and correlations between annual cycles of the variables. In particular, processes operating on different timescales with respect to stream salinity and salt export were identified.

Stable water isotopes

Stable water-isotope analyses of groundwater samples were used to assist in understanding the process of salt accumulation in groundwater. The isotope analysis was performed by the CSIRO Land and Water Isotope Analysis Service in Adelaide, South Australia. The ratios of the heavy to light isotopes of oxygen ($^{18}O/^{16}O$) and hydrogen ($^{2}H/^{1}H$) in the water samples were normalized to Vienna Standard Mean Ocean Water (vs. V-SMOW) in per mill (‰) difference using delta (δ) notation. The precision of ^{18}O analysis was 0.15‰ for natural abundance and 0.4‰ for enriched water, while the precision of ^{2}H analysis was 1‰ for natural abundance and 3‰ for enriched water.

The local meteoric water line (LMWL) for Adelaide, the nearest station with isotope records, was determined as:

$$\delta^{2}$$
H = 7.95 δ^{18} O + 11.60 versus V - SMOW (1)

This equation is in good agreement with meteoric water lines calculated for Bedford Park ($\delta^2 H = 7.54\delta^{18}O + 11.2$) and Flagstaff Hill ($\delta^2 H = 7.44\delta^{18}O + 11.97$) at the western foothills of the Mt Lofty Ranges (Kayaalp 2001). The overall and monthly mean isotopic signatures of Adelaide precipitation were calculated by weighting each isotope value by the corresponding proportion of total precipitation represented.

Hydrochemistry

Hydrochemical data were used to identify the sources and evolution of dissolved salts in groundwaters and streams. Chemical analysis of surface water samples was performed by CSIRO Land and Water in Adelaide and additional samples for the Bremer River and groundwater were gathered from other sources. The accuracy of all chemical analyses was checked using the ion charge balance equation shown in Eq. (2).

$$E = \frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} \times 100$$
(2)

The reaction error (E) of all groundwater samples was less than the accepted limit of 5% and samples where E was greater than 5% were eliminated from subsequent analyses. However, for the surface water and Bremer River samples, just over two-thirds of the samples had E values less than 5%, with the remaining samples having E values generally less than 10%. Given the number of sources from which this data is collected, it is very encouraging that the majority of all samples meet the general reaction error limits, or just marginally exceed it. Importantly, the hydrochemical interpretations made here do not appear to be affected by whether samples with E values marginally greater than 5% are excluded or not.

Regular hydrochemical sampling over 6 years (1995-2002) of the Bremer River (near Hartley), downstream of the two upland catchments, provided an excellent data set with which to estimate the sources and relative contributions of individual ions to the combined salt export from the two upland catchments. The contributions of salt from marine and rock mineral weathering sources were distinguished and quantified, assuming the conservative behaviour of chloride, by calculating the amount of each ion attributed to seawater based on a linear seawater dilution relationship. The contribution of seawater was then subtracted from each measured ion and from the TDS to produce estimates of the salts that could not be attributed to seawater. The equation used to calculate the amount of each ion derived from weathering sources can be presented as:

$$(X)_{weathering} = (X)_{sample} - \frac{(X)_{seawater}}{(Cl)_{seawater}} \times (Cl)_{sample}$$
(3)

Where X is the concentration (mg/L) of the ion in the sample and in seawater and Cl is the concentration (mg/L) of chloride in the sample and in seawater. The percentage of the measured ion that could be attributed to rock weathering was then calculated as:

$$(X)_{\text{%weathering}} = \frac{(X)_{\text{weathering}}}{(X)_{\text{sample}}} \times 100$$
(4)

The percentage of the TDS represented by the total concentration of each ion in solution was then calculated as:

$$(X)_{\text{\%TDS}} = \frac{(X)_{\text{sample}}}{\text{TDS}_{\text{sample}}} \times 100$$
(5)

Hydrogeology Journal (2006) 14: 1339-1359

Spatial interpretation

Groundwater and stream data were interpreted spatially by interpolation using ESRI ArcGIS version 8.1 GIS software. Sample points must be of sufficient distribution and density for interpolation to accurately represent the variation of the measured parameter. The topography of the Bremer River catchment is heterogeneous on a much smaller scale than the spatial resolution of the samples used in this study. Therefore, the interpolated surfaces were useful to illustrate the spatial distribution of measured values rather than a prediction of the parameters at unsampled locations. Considering the spatial distribution of data and the intention of the interpolation, the deterministic and relatively straightforward inverse distance weighted (IDW) methodology was chosen. While groundwater can usually be considered as a continuous surface, stream networks are restricted to valley depressions and are thus not spatially continuous. In order to preserve their linear network, the interpolated surface of stream salinity was restricted to the catchment drainage lines. All raster grid cell values not intersecting a stream were eliminated by multiplying the interpolated stream salinity with the catchment drainage lines. A grid cell size of 200×200 m was used for the purpose of providing sufficient visualization at the whole catchment scale. The grid may therefore be interpreted as an indication of the likely stream salinity along drainage lines in the study area based on the values of measured stream salinity.

Streamflow hydrograph separation

Daily stream hydrographs from the Dawesley Creek, Mt Barker Creek and Bremer River were separated into baseflow and quickflow components in order to determine the contribution of groundwater to streamflow. Baseflow was defined as the slow response of groundwater discharge from the saturated and unsaturated subsurface zones, while quickflow was defined as the rapid response of rainfall-generated surface runoff and flow through the unsaturated subsurface zone. The hydrograph separation technique used is a subroutine (HYBASE) in the time series data management program HYDSYS (1992), which applies the recursive digital filter algorithm of Lyne and Hollick (1979). An evaluation of automated hydrograph separation techniques (Nathan and McMahon 1990) found the Lyne and Hollick filter to be a fast and objective method of continuous baseflow separation, producing similar results to the traditional graphical techniques. It is recognized, however, that the main value in using this technique in this study is to provide a qualitative demonstration of the relationships between streamflow, salinity and salt load rather than a quantitative physical interpretation. In particular, bank storage of water in the alluvial aquifer during peak flows is not explicitly recognized. This means that baseflow could be overestimated during periods of high flow.

This filter algorithm has been widely applied to daily streamflow data and is cited in much of the Australian rainfall-runoff modelling literature (Grayson et al. 1996). Based on the theory of signal processing, the procedure separates the streamflow hydrograph into low frequency (baseflow) and high frequency (quickflow) components using a digital filter of the form:

$$f_{k} = \alpha f_{k-1} + \frac{(1+\alpha)}{2} (y_{k} - y_{k-1})$$
(6)

where f_k is the filtered quickflow response of streamflow at the kth sampling instant, yk is the original streamflow measurement, and α is the filter parameter. The filtered baseflow component of streamflow is thus defined as y_k -f_k. Using data from 186 catchments in south-eastern Australia, Nathan and McMahon (1990) showed that the most acceptable baseflow separation was achieved with a filter parameter α =0.925, although acceptable results were obtained in the range of 0.9–0.95. Physical conditions and streamflow characteristics in the eastern Mt Lofty Ranges were considered to be consistent with the findings of that assessment. The filter parameter affects the degree of attenuation, while the number of passes of the filter determines the degree of smoothing. The original work of Lyne and Hollick (1979) and the subsequent evaluation by Nathan and McMahon (1990) showed that three filter passes (forward, backward and forward again) produced the best results.

For this study, a filter with a 60-min interval was passed over the streamflow data three times using a filter parameter of 0.925. The output was constrained so the separated baseflow and quickflow components were not negative or greater than the original streamflow. Missing values in the data were interpolated in HYBASE with a straight line joining measured values on either side thus minimizing the propagation of error resulting from zero values. The proportion of baseflow was calculated as the ratio of calculated baseflow component to the total streamflow, while the ratio of baseflow to quickflow was used to represent the relative contributions of each component.

Stream salt-load calculation

The salt mass or load discharged from a stream for a given time is equal to the product of the streamflow and the corresponding stream-water salinity as total dissolved solids (TDS) concentration. Stream salinity was measured as electrical conductivity (EC). The TDS was estimated from a linear regression of EC and TDS measurements for the Bremer River. The conversion factor of 0.63 for EC to TDS from the regression (correlation coefficient R^2 =0.99) is within the common range of 0.54 – 0.75 for natural waters (Hem 1982).

A least squares regression of streamflow and calculated salt-load data was used to estimate salt load where stream EC data were missing. The processed data set consisted of daily values for which corresponding streamflow and EC values existed during the 6-year period of mid-1997 to 1347

$$Saltload = e^a \times flow^b \tag{7}$$

The coefficients *a* and *b* are values determined from the regression output. For the Mt Barker Creek a=0.641 and b=0.868 (R^2 =0.98) and for the Bremer River near Hartley a=0.893 and b=0.882 (R^2 =0.98). The 95% confidence interval for the prediction is approximately plus and minus two times the standard error and is defined as:

$$\begin{aligned} \text{Saltload}_{\text{upper95\%}} &= e^{a} \times \text{Flow}^{b} \times (e^{2})^{\text{S}} \\ \text{Saltload}_{\text{lower95\%}} &= e^{a} \times \text{Flow}^{b} \times (e^{2})^{-\text{S}} \end{aligned} \tag{8}$$

Where S is the standard error for the regression (S=0.219 for Mt Barker Creek; S=0.256 for Bremer River near Hartley).

Results and discussion

The results are presented here in a way that builds a holistic picture of groundwater and stream salinity characteristics at the whole catchment scale, illustrating some of the key factors that explain the sources and occurrence of saline groundwater and the mechanisms by which this manifests as saline streamflows and salt export out of the catchment.

Origin of salts

Salt may be derived from accumulated marine salts deposited in the catchment by rainfall over thousands of years prior to human disruption or salt may also be derived from in situ weathering of rock minerals from specific salt-bearing formations. This has sparked considerable debate as to the primary source of dissolved salts. Authors have cited terrestrial sources (Gunn and Richardson 1979; Acworth and Jankowski 2001) and others marine salt (Jones et al. 1994; Herczeg et al. 2001). Both sources may contribute to a greater or lesser extent depending on local factors including geology, rainfall, proximity to the coast and human disruptions to the hydrological regime.

Quantitative hydrochemical data presented here show that marine salts were the primary source in the Bremer River catchment, but a significant contribution was also made by weathering of sulfate and bicarbonate bearing rock minerals. Recent work by Smitt et al. (2004) in the eastern Mt Lofty Ranges has indicated that dissolved salts are primarily of marine origin and only a small component came from rock-mineral weathering. A seawater source for the majority of dissolved salts in the Bremer River Catchment is consistent with the current understanding of the source of salt in the Murray Basin (Herczeg et al. 2001) and the Wheatbelt of Western Australia (Salama et al. 1993). Additional hydrochemical data are presented as 1348

Fig. 4 Deuterium vs. oxygen-18 data for groundwater from the Bremer River catchment (Radke et al. 2000), plotted with the amount-weighted mean signature of Adelaide rainfall and the winter (May-October) and summer (November-April) variability. The Adelaide local meteoric waterline ($\delta^2 H = 7.9525\delta^{18}$ O + 11.604% o v SMOW) was calculated using rainfall with $\delta^{18}O$ of less than -2%(V-SMOW). Isotopes in rainfall sourced from the IAEA Global Network of Isotopes in Precipitation online database (IAEA 2001)



a result of this study and the findings are in agreement with these previous studies and provide a significant contribution to understanding the origins of the total catchment salt export.

Stable water isotope evidence

The stable water isotope composition of groundwater was very similar to that of amount-weighted mean precipitation (Fig. 4) indicating that groundwater was directly recharged by rainfall. Oxygen-18 and deuterium in groundwater samples ranged from -5.35 to -4.28‰ δ^{18} O and -31.2 to -25.4‰ δ^{2} H (vs. V-SMOW), compared to the amount weighted mean signature of Adelaide rainfall of -4.5% δ^{18} O and -24.57% δ^{2} H (vs. V-SMOW). The absence of significant isotopic enrichment away from the meteoric waterline showed that recent evaporation was a minor process in the evolution of salts in relatively fresh groundwater (1,200-4,500 mg/L TDS). For groundwater to obtain much greater TDS than would be obtained from rainwater (bringing seawater salts), there must be a large loss of water with retention of salts in the soil. The most obvious mechanism to explain this occurrence without changing the isotopic composition of the water is by plant transpiration. This concept is consistent with the model presented to explain the longterm accession of marine salts prior to clearance of native vegetation.

It is noted that the isotope data do not represent the range of groundwater salinities encountered in the Bremer River catchment and it is not known whether evaporative concentration would play a more significant role in salt accumulation under certain local circumstances such as where groundwater is very shallow.

Hydrochemical evidence

The chemical composition of groundwater and stream samples was distinctly chloride and sodium dominant, very similar to local rainwater and approaching that of seawater. Plots of selected ions vs. the conservative chloride ion (Fig. 5) showed relationships that mostly followed the seawater dilution line except for sulfate and bicarbonate which were consistently elevated above the expected seawater contribution.

Sodium vs. chloride (Na-Cl, Fig. 5a) and bromide vs. chloride (Br/Cl, Fig. 5b) showed clear trends along the seawater dilution line for both groundwater and streams. The Br/Cl plot is the more conclusive indicator of the salt source because, unlike the Na/Cl plot, the lines for halite dissolution and seawater dilution are distinctly different. The Br/Cl ratio ranged from 1.26×10^{-3} to 1.82×10^{-3} and samples were distributed around and slightly below the seawater ratio of 1.54×10^{-3} over the range of chloride concentrations. In comparison, waters affected by dissolution of evaporites (e.g. halite) have low Br/Cl ratios ranging from 1×10^{-3} to 1×10^{-4} (Davis et al. 1998). The Br/Cl ratios of some samples were lower than seawater but much higher than halite (1×10^{-4}) indicating that evaporite dissolution or rock weathering contributed a small amount of salt. The analytical error in the bromide determination of 0.6 µmol/L is small compared to the deviation of some of the samples from the seawater dilution line.

Na/Cl ratios of groundwater and streams ranged from 1.14 to 0.82, clustering around and slightly above the seawater ratio of 0.86 over the range of chloride concentrations. Some samples at higher chloride concentrations plotted near the Na/Cl trend that would result from dissolution of halite. The higher sodium than the seawater dilution line could be related to additions of dissolved solids with a high Na/Cl ratio from weathering



Fig. 5 Chemical plots for groundwaters (GW; 1995) and streams (SW; 2002) in the Bremer River catchment and the Bremer River near Hartley (1995–2001), showing the relationship of chloride to **a** sodium, **b** bromide, **c** carbonate and **d** sulfate. *Solid lines* show dissolution of seawater and seawater ratios; *Dashed lines* shows dissolution of halite with Na/Cl and Br/Cl of 1 and 10^{-4} respectively. Groundwater data sourced from (Radke et al. 2000), stream data sourced from CSIRO data (Walker et al. 2004; Cox et al. 2002a) and Bremer River data sourced from the Environmental Protection Agency (EPA 2000)

of metasedimentary rocks and from cation exchange. Bedrock in the study area was deposited in marine conditions and, providing it has not undergone substantial flushing by fresh groundwater, the clay-rich weathering products could still contain substantial adsorbed sodium. It is possible that as carbonate minerals in the metasedimentary rocks dissolve and the resultant groundwater with a relatively high (Ca+Mg)/Na ratio flows through the rocks, a softening of the water could occur to produce Na-HCO₃ type waters. Bicarbonate concentrations significantly elevated above the seawater line (Fig. 5c) support this concept and indicate a mineral weathering contribution from formations such as limestone. Similarly, sulfate (Fig. 5d) was consistently above the seawater line in the lower Bremer River and reached levels of up to eight times that of the seawater dilution in other streams, mostly at the dilute end of the spectrum.

The percentage of water chemistry that could be attributed to rock weathering and the relative contribution of each ion as a percentage of the TDS are presented in Fig. 6. The calculations showed that on average, 25% of the total salt exported from the Bremer River catchment

was derived from sources other than seawater. This estimate was in good agreement with the preliminary finding of Cox et al. (2002a) that the contribution from rock sources could be as much as 25% of total salt. Except for a small amount of sodium (6%), the dominant ions chloride and sodium were not derived from rock weathering. Sulfate and bicarbonate were the major contributors to weathering derived salts. Concentrations of sulfate and bicarbonate were consistently elevated above the seawater contribution and on average 49% of sulfate and 97% of bicarbonate exported from the Bremer River catchment were derived from rock weathering sources, amounting to about 18% of the total salt export.

The stream samples with exceptionally elevated sulfate and bicarbonate indicated that salts derived from mineral weathering were derived from discrete sources in the landscape. An example was provided by one stream sample from the Dawesley Creek in the lower reaches of the MBC subcatchment for which sulfate and bicarbonate were 30% (630 mg/L) and 28% (591 mg/L) of the TDS (2,140 mg/L) respectively. Bicarbonate in another sample in this area accounted for 21% (219 mg/L) of the TDS **Fig. 6** Percentage of the TDS attributed to rock weathering and the relative contribution of each ion, based on the conservative behaviour of the chloride ion. Computed as the difference from the expected seawater dilution line (as described in text)



(1,043 mg/L). The data available to this study were insufficient to establish an explicit link between ground-water salinity and surficial geology. However, there is an apparent correlation between the elevated concentrations of these ions in groundwater and the occurrence of sulfidic deposits and limestone formations, which may be contributing a component of dissolved salts.

Factors explaining groundwater salinity

The general range of well depths in the different areas from which groundwater salinity samples have been collected (Fig. 7) shows that salinity can range widely in wells of less than about 130 m depth. Elevated salinity levels in some wells within this zone suggests an open system in which vertical water exchange can occur, allowing for the downward migration of accumulated salts. Elevated salinity levels were not measured in any wells deeper than about 130 m, suggesting that below this depth, there is reduced exchange of water with the surface system. The vertical extent of high salinity groundwater is approximately consistent with the maximum 100 m expected depth of the alluvial aquifer system overlying bedrock. This system will be deepest in local basins and valleys so it is suggested that these are the areas where the vertical extent of saline groundwater can be expected to be greatest.

There was a high degree of spatial variability in groundwater salinity across the catchment (Fig. 8), with values ranging between 0.5 and 25 mS/cm EC and a mean value of 4 mS/cm EC. Average annual rainfall and geology were found to be two important factors contributing to an explanation of the observed spatial distribution of groundwater salinity.

Rainfall

The strong eastward rainfall gradient across the catchment is an important factor in understanding the current state of groundwater salinity. Except for areas in the MBC subcatchment where specific geological formations resulted in high groundwater salinity, the higher rainfall in the western portion of the catchment (Fig. 2) has resulted in overall lower groundwater salinity (<4 mS/cm) than neighbouring subcatchments. A distinct zone of fresher groundwater existed along the MBC near the outlet of the catchment, suggesting that water loss from the creek could be contributing to localized recharge of fresh groundwater.

Studies in Western Australian catchments have shown that, since clearing, salt storage and stream salinity are inversely proportional to the amount of annual rainfall (Schofield and Ruprecht 1989). The findings of this study are consistent with this observation, showing much higher stream salinity in the lower rainfall subcatchment (UBR) than in the higher rainfall subcatchment (MBC). While, on



Fig. 7 Groundwater salinity vs. bore depth for bores in the Bremer River catchment



the other hand, the rate of salt export following clearing is proportional to the amount of annual rainfall received by a catchment (Jolly et al. 2001). In the higher rainfall zone to the west, more rapid mobilization and export of stored salts has generated a zone of relatively less saline groundwater in the MBC subcatchment. This indicated that the MBC subcatchment is more advanced in the salt export cycle relative to the neighbouring subcatchments. A study by Jolly et al. (2000) found decreasing stream salinity trends in the Dawesley and Mt Barker Creeks and suggested that the MBC subcatchment has in fact passed the peak of salt export.

Geology

Areas where groundwater was more saline than about 8 mS/cm EC, mostly occurred in the highly altered Kanmantoo Group metasediments (Figs. 3 and 8) and include the Backstairs Passage, Carrickalinga Head and Tunkalilla formations and Talisker Calc-Siltstone, which originated in a shallow marine environment conducive to the development of saline sulfidic deposits as reported by (Fitzpatrick et al. 1996). The Tunkalilla Formation, outcropping in the south of the Bremer River catchment, is a black pyritic shale that has also been linked with salinity in the region (Henschke 1997).

It has been suggested (Pannewig 1992) that the laminated sandstones and siltstones of the Backstairs Passage Formation contain minerals such as albite and biotite that weather to release salts into the groundwater. Albite is a sodium aluminium silicate belonging to the feldspar group of minerals, while biotite is a common rock forming mineral with a layered structure of iron magnesium aluminium silicate sheets weakly bonded together by layers of potassium ions. It is possible that weathering of these minerals contributes to the weathering component of dissolved salts.

It should also be noted that the chosen interpolation method used in visualizing the data in Fig. 8 (inverse distance weighting) tends to produce bulls-eye structures where the data are not uniformly distributed. Other techniques such as kriging may have resulted in a better presentation. Nonetheless, whilst the links between groundwater salinity and geology cannot be properly quantified without more specific data on the composition of dissolved salts, the available data (irrespective of the contouring algorithm) suggests salinity hotspots are connected with particular geologic formations. This interpretation may still be biased by the non-uniform distribution of EC sampling points in the different geologic formations.

The high variability of groundwater salinity in the Bremer River catchment indicated that salt mobilization and leaching has occurred heterogeneously in the landscape. However, the exact cause of groundwater salinity 'hotspots' (EC >8 mS/cm) has not been fully identified. While evaporative concentration of salt in shallow groundwater seems the most obvious explanation for the salinity 'hotspots', it is peculiar that it occurs in a distinct north–south orientation and this may be indicating a particular role of geology. It is possible that sulfidic siltstones and pyritic shales outcropping in these areas contribute to elevated groundwater salinity levels, but given the small proportion of the TDS represented by sulfate and bicarbonate, the extent to which this occurs is likely to be minimal.

Dynamics of stream salinity and salt loads

With relatively high mean groundwater salinity throughout the Bremer River catchment it was assumed that high stream salinity and salt loads would result wherever groundwater physically intersected a stream channel, the base of which may be 0–4 m below ground level, depending on the degree of channel erosion. Temporal variation in groundwater levels such as seasonal fluctuations, may result in variations in the extent of discharging groundwater. However, the present data set was not sufficient to achieve this level of detail.

Groundwater influence on stream salinity

A spatial interpretation of groundwater depth data (Fig. 9) indicated that there was an extensive area of shallow groundwater (depth to water <4 m) across the eastern side of the UBR subcatchment. Groundwater was deeper than 10 m across the greater part of the MBC subcatchment, but there were some records of shallow groundwater. This interpretation is useful to visualize the measured data, but it does not adequately represent the expected spatial variability of groundwater depth at the local scale. This seemed to be the most likely explanation for the apparent isolation of scattered shallow groundwater measurements. That is, the distribution of points for groundwater level measurement near (shallower depths to groundwater) or at a distance (potentially greater depths to groundwater) from streams and rivers would have a substantial influence on the pattern in Fig. 9.

Stream salinity (EC) was variable within a range of 0.5 to 10 mS/cm and high values of EC correlated with areas of high groundwater discharge potential, as shown by the interpolation of stream salinity along drainage lines (Fig. 10). In particular, shallow groundwater and high stream salinity were apparent in an extensive area of the eastern UBR subcatchment and smaller areas in the north and south of the MBC subcatchment. Groundwater was deep and streams were less saline (<3 mS/cm) across most of the MBC subcatchment and the uppermost portion of the UBR subcatchment. The mean salinity of stream discharge from the subcatchments, calculated from daily records, supported the observed spatial distribution of stream salinity. Discharge from the UBR subcatchment was 7.90 mS/cm, while that of the MBC subcatchment was 2.88 mS/cm and the combined downstream discharge in the Lower Bremer River was 3.30 mS/cm. This confirmed that the widespread occurrence of saline streams in the UBR subcatchment was contributing to overall higher discharge salinity than that of the neighbouring, higher rainfall MBC subcatchment.

Streamflow and salinity relationships

Due to the climate of the study area, the streams generally only have large flows in direct response to rainfall events, with 90% of annual flow in all streams occurring during the winter months between May and October. During other times, the main source of flow is from groundwater discharge as baseflow. This pattern is illustrated graphically in Fig. 11, which shows at a glance the relative contributions of baseflow and quickflow to the total volume of streamflow at the daily scale, and clearly characterizes the Mt Barker Creek as a baseflow dominated stream. Figure 11 also shows that high flows are typically quickflow dominant, but it is important to note that the baseflow/quickflow ratio is independent of flow volume, therefore with some small rainfall events, or in the early stages of a large event, it is possible to have quickflow dominance at low flows. The daily data showed that baseflow dominated streamflow 80-90% of the time and contributed 40-50% of the annual streamFig. 9 Spatial distribution of groundwater depth; inverse distance weighted interpolation from 140 single and mean values collected between 1992 and 2002. Data compiled from Primary Industries and Resources of South Australia (PIRSA 2002), Bremer Barker Catchment Group, 2002, personal communication and Department of Water, Land and Biodiversity Conservation online database system "Obswell" (DWLBC 2002)



flow volume. When considered volumetrically, baseflow was directly proportional to the volume of streamflow and thus 90% of baseflow occurred during the winter months of May to October when groundwater is displaced by rainfall. This is also the period when most of the stream salt load is generated. However, when considered as a proportion of streamflow, the baseflow contribution was highest in times when rainfall is absent. This is the sustained low-volume discharge of groundwater that constituted up to 100% of streamflow, typically during summer.

The relationships between stream salinity and the volume and sources of flow are illustrated graphically in Fig. 12. It is evident from the data that there are a number of factors influencing the dynamics of stream salinity fluctuations. These are driven by the occurrence of rainfall generated quickflow and baseflow generated from ground-water discharge. Figure 12b shows that in the absence of



Fig. 10 Spatial distribution of stream salinity (*EC mS/cm*); inverse distance-weighted interpolation from 76 single and mean values collected between 1990 and 2002. Data compiled from Bremer Barker Catchment Group, 2002, personal communication, SA Water, 2002, personal communication and Waterwatch, 2002, personal communication

rainfall-generated quickflow (i.e. a high baseflow/quickflow ratio) the salinity of streamflow approaches a value within the range of about 1.8–2.8 mS/cm, which can be inferred to be the average salinity of shallow alluvial groundwater contributing to streamflow in the MBC subcatchment. Although streamflow data were not available for the UBC catchment it is expected that the average salinity of baseflow in the Upper Bremer River would be considerably higher, due to the higher average salinity of total streamflow (7.91 mS/cm). While Fig. 12a shows that when rainfall generates streamflow above the very low flow (i.e. close to zero) conditions prevalent for most of

Fig. 11 Daily streamflow vs. daily baseflow/quickflow ratio in the Mt Barker Creek (1997– 2002) plotted on a log–log scale. Equal contribution of baseflow and quickflow is indicated by the *dotted line*. Automated daily stream sampling data from station AW426557 sourced from the Department of Water, Land and Biodiversity Conservation online database system (DWLBC 2002)



the time, stream salinity remains low. However, when streamflow is very low (Fig. 12a) and/or quickflow is an appreciable portion of flow (Fig. 12b), stream salinity is highly variable.

The large variability in stream salinity observed in the low flow or quickflow dominant data can be explained conceptually as being a result of two primary mechanisms. Firstly, there is a 'first-flush' effect caused by mobilization of salts that have accumulated both in-stream and in/on the soil adjacent to the stream channel by evaporative losses of stream water or near-surface groundwater. This mechanism is active in the early stages of a rainfall event, particularly when it has been preceded by an extended dry period, and it explains the occurrence of quickflow dominance in coincidence with elevated stream salinity as shown in Fig. 12b. The first-flush effect would be most pronounced at times when rainfall occurs after an extended dry period, and would be small or negligible during winter after many rainfall events have already flushed away any accumulated salts. An examination of the flow hydrograph showed that the first-flush effect was evident for up to 3 days following the initial streamflow increase. Secondly, there is a process of in-stream evaporative concentration of salts during dry periods



Fig. 12 Scatter plots of daily mean stream salinity (EC) vs. **a** daily streamflow and **b** daily baseflow/quickflow ratio in the Mt Barker Creek (1997–2002). Note that a baseflow/quickflow ratio of 1 represents equal contributions of the two flow components. Automated daily stream sampling data from station AW426557 sourced from the Department of Water, Land and Biodiversity Conservation online database system (DWLBC 2002)

when flow is low and the residence time of water in the stream is likely to be quite long. This mechanism could explain the occurrence of stream salinities that are elevated above the expected salinity contribution of groundwater at low flows as shown in Fig. 12a.

The first peakflow waters would also be the water that would most easily enter the alluvial aquifer as bank storage during the period when the hydraulic head in the stream was higher than that of the groundwater in the adjacent alluvial aquifer. Thus, an influx of relatively saline water could enter the alluvial aquifer and then later be released during the recession phase of the flow events. This process would have an effect on the distribution of points on the flow vs. salinity graphs, but it has not been investigated in detail in this work. The daily time-step of the data and large areal extent of rainfall contribution to streamflow were also limitations to a more detailed interpretation of the streamflow and salinity dynamics.

Salt-load analysis: a practical technique for targeted management

The mean annual salt load from the upland subcatchments of the Bremer River (MBC and UBR) was calculated using the available data and the salt-load prediction relationship (Fig. 13) for the station on the Lower Bremer River (AW426533). The total salt export was about 24,500 tonnes, 80% of which occurred between July and September when both streamflow and baseflow were highest. Confidence in predicted salt load decreased at higher flows due to more variable salt load and limited



Fig. 13 Regression of salt load vs. streamflow in the Lower Bremer River (1973–2002), showing measured salt load, predicted salt load and the 95% confidence interval for the prediction, plotted on a log-log scale. Salt load calculated as the product of daily streamflow and TDS (derived from EC). Automated daily stream sampling data from station AW426533 sourced from the Department of Water, Land and Biodiversity Conservation online database system (DWLBC 2002)

occurrence of large events. According to Williamson et al. (1987), who studied a similar cleared catchment in the Western Australian Wheatbelt, the non-linearity of the prediction relationship represented the baseflow contribution to stream salt load. That is, at lower flows, the larger proportion of baseflow caused elevated salt loads relative to streamflow volume, while at high flows, the larger volume of quickflow reduced the relative contribution of baseflow and thus salt. However, in terms of the total mass of exported salt, the vast majority occurred during periods of high flows generated by winter rainfall.

The contribution of each subcatchment to the total salt export is dependent on the degree of groundwater–stream interaction, the salinity of groundwater and also the amount of rainfall received by each subcatchment. The dynamics of salt-load generation identified in this study, indicate that discharge of saline groundwater to streams provides the salt load, while rainfall-generated high flow volume is the main driver of salt export. This is in agreement with the findings of Williamson et al. (1987).

It has become evident from this study that undertaking salt-load analysis for individual subcatchments within a larger catchment area could provide a practical, low-cost technique to identify areas of high salinity at which to target further investigations and eventual management. Instrumentation of streams to measure flow and salinity at the subcatchment outlets can enable easy identification of the relative contributions of each subcatchment to the total salt export without the need for exhaustive and costly studies of groundwater conditions and interactions with streams. Such investigations would be better targeted at known problem areas in order to develop the information necessary for ameliorative intervention.

The relative contributions of salt load from each of the subcatchments in this study could not be quantified because there was insufficient streamflow and salinity monitoring instrumentation. In particular, there was no flow or salinity instrumentation in the RRC subcatchment, there was no flow instrumentation in the UBR subcatchment and, although the MBC subcatchment had both flow and salinity instrumentation, the flow meter was placed midway through the subcatchment rather than together with the salinity instrumentation at the downstream end of the subcatchment. These critical data gaps need to be addressed in order to progress salinity management objectives in the study area.

Effect of temporal data resolution on interpretation

The hydraulic data used in this study, including streamflow and salinity, allowed relationships that drive short-term trends and fluctuations in stream salinity and salt loads to be identified. This study has established that, in order to develop an accurate understanding of these relationships, it is critical that the data are collected and assessed on an appropriate timescale. This is particularly pertinent to fluctuations in streamflow, salinity and salt load which typically occur in response to individual rainfall events, but is also broadly relevant to time variable data in general.

Figure 14 illustrates the effect of averaging rainfall, streamflow, stream salinity and stream salt load at the 1day, 7-day and 30-day timescales over the annual cycle of 1998 for the stream gauging station on the Mt Barker Creek and rainfall at Mt Barker. Daily data showed that stream salinity was highly variable and fluctuated in direct response to streamflow events. In particular, with the onset of rainfall and subsequent streamflow, an initial increase in stream salinity was evident, indicating a salt wash-off effect, followed by a sharp drop as high rainfall-generated flows dominated. A smearing effect of daily variability is clearly seen with 7-day averages and the short timescale are completely lost in the 30-day averages. The 30-day averaging of the data gives the impression that streamflow and salinity are largely unrelated, when the two are actually in a close cause and effect relationship. This time-dependent characteristic of the stream parameter responses implies that care must be exercised in the manipulation of daily data to avoid the inadvertent loss of information resulting from smoothing of short timescale relationships due to averaging or inadequate data resolution. It is evident that the use of daily values (or more frequent) is the most valuable to identify streamflow and salinity dynamics, particularly where data are to be used to

develop prediction relationships to patch up gaps in measured data sets.

Conclusion

The key focus of this research was to use a wholecatchment scale approach to assess spatial and temporal patterns of groundwater and stream salinity and salt sources, with the aim of enabling more targeted investigations and management at problem areas. Data encompassing multiple subcatchment areas extending across approximately 520 km² of the eastern Mt Lofty Ranges have been systematically compiled and analysed using an integrated suite of tools including GIS, hydrograph separation and hydrochemical techniques.

The key conclusions of this study are:

 Additional hydrochemical data supported the findings of previous work in the eastern Mt Lofty Ranges (Smitt et al. 2004) that most (75%) dissolved salts were of marine origin and about 25% could be attributed to terrestrial sources such as rock mineral weathering. Stable water isotopic data indicated that salt accumu-



Fig. 14 Averaging of rainfall, streamflow, stream salinity and stream salt-load data at 1-day, 7-day and 30-day timescales from the Mt Barker Creek stream gauging station and Mt Barker township rainfall data

lation primarily occurred by plant transpiration of water. Importantly, this study has provided an integration of salt loads from upland catchments of the Bremer River and quantified the major ionic composition of total salt export from the upland area.

- 2. The spatial distribution of groundwater salinity across the subcatchments showed an inverse correlation with average annual rainfall, and salinity 'hotspots' also appeared to be related to certain geological features in the landscape, although the latter have not been fully defined.
- 3. Areas of elevated stream salinity showed a clear correlation with areas of shallow groundwater indicating the contribution of baseflow to streams, and this contribution was the driver of salt export from the catchment, which primarily occurred during the winter months of high rainfall.
- 4. Stream salinity fluctuations were controlled by the baseflow/quickflow ratio and were largest during low-flow conditions. The cause of this variability was attributed to a 'first-flush' effect in the early stage of some rainfall events and to in-stream evaporative concentration of salt during dry periods. The increase in stream salinity prior to the dominance of rainfall-generated low salinity flows was observed to last for up to 3 days.
- 5. It is critical that the data are collected and assessed on an appropriate timescale in order to develop an accurate understanding of streamflow, salinity and salt-load relationships. Daily data shows a clear relationship between rainfall, streamflow and stream salinity. As the analysis timescale increases from one day to seven days and finally to 30 days, these trends and relationships become substantially less discernible.
- 6. Salt-load analysis for individual subcatchments within a larger catchment area could provide a practical, lowcost technique to identify areas of high salinity at which to target further investigations and eventual management.

The integration of hydraulic and hydrochemical data in a multi-disciplinary approach provides a large-scale understanding of the origins of salt as well as the spatiotemporal patterns of stream salt loads and catchment salt exports. This study clearly demonstrates the usefulness of employing regional scale databases in hydrogeologic analyses. Large-scale analyses such as those presented here should be complimented by more localscale analyses in targeted problem areas in order to validate and compare results at each scale and develop the level of understanding necessary for management. Such a comparison would also provide useful insights into current challenges faced in hydrologic scaling.

References

- Acworth RI, Jankowski J (2001) Salt sources for dryland salinity: evidence from an upland catchment on the Southern Tablelands of New South Wales. Aust J Soil Res 39:39–59
- Hydrogeology Journal (2006) 14: 1339–1359

- Blackburn G, McLeod S (1983) Salinity of atmospheric precipitation in the Murray-Darling Drainage Division, Australia. Aust J Soil Res 21:411–434
- Cox JW, Ashley R (2000) Water quality of gully drainage from texture contrast soils in the Adelaide Hills in low rainfall years. Aust J Soil Res 38:959–972
- Cox J, Fritsch E, Fitzpatrick R (1996) Interpretation of soil features produced by ancient and modern processes in degraded landscapes. 7. Water duration. Aust J Soil Res 34:803–824
- Cox J, Spouncer L, Davies P (1999) Water and soil degradation in the Keynes Catchment, South Australia: 2. Electrical conductivity, pH and chloride concentrations of the regolith. 40/99, CSIRO Land and Water, Adelaide
- Cox J, Kerryn McEwan, Phil Davies, Smitt C, Herczeg A, Walker G (2002a) Salt Transport in the Bremer Hills, SA: Report for NAP South Australian salt mapping and management. 50/02, CSIRO Land and Water, Adelaide
- Cox JW, Chittleborough DJ, Brown HJ, Pitman A, Varcoe JCR (2002b) Seasonal changes in hydrochemistry along a toposequence of texture-contrast soils. Aust J Soil Res 40:581–604
- Davis SN, Whittemore DO, Fabryka-Martin J (1998) Uses of chloride/bromide ratios in studies of potable water. Ground Water 36(2):338
- Department of Water, Land and Biodiversity Conservation (DWLBC) online database system "Obswell". http://www. dwlbc.sa.gov.au/water/groundwater/obswell.html. Accessed Dec 2002
- Ecker S (1998) Ground water modelling and salt balance analysis to determine target areas for recharge reduction in the Bremer Catchment. MSc Thesis, The University of Adelaide, Adelaide, pp 80
- Environmental Protection Agency (EPA) (2000) The state of health of the Mt Lofty Ranges catchments from a water quality perspective. EPA, Dept of Environment and Heritage. Government of South Australia, pp 28
- Fitzpatrick R, Fritsch E, Self PG (1996) Interpretation of soil features produced by ancient and modern processes in degraded landscapes. 5. Development of saline sulfidic features in non-tidal seepage areas. Geoderma 69:1–29
- Grayson RB, Argent RM, Nathan RJ, McMahon TA (1996) Hydrological recipes: estimation techniques in Australian hydrology. Cooperative Research Centre for Catchment Hydrology, Canberra
- Gunn RH, Richardson DP (1979) The nature and possible origins of soluble salts in deeply weathered landscapes of Eastern Australia. Aust J Soil Res 17:197–215
- Hem JD (1982) Conductance: a measure of dissolved ions. In: Minear RA, Keith LH (eds) Water analysis, vol 1, Inorganic species, part 1. Academic Press, New York
- Henschke CJ (1997) Dryland salinity management in the Mt Lofty ranges. 254, Primary industries South Australia
- Herczeg AL, Dogramaci SS, Leaney FWJ (2001) Origin of dissolved salts in a large, semi-arid ground water system: Murray Basin, Australia. Mar Freshw Res 52:41–52
- HYDSYS (1992) Time series data management program. Hydsys Ltd, Canberra
- IAEA (International Atomic Energy Agency) (2001) Global network of isotopes in precipitation online database. http:// www.isohis.iaea.org/. Accessed 2002
- Jolly I, Walker G, Stace P, van der Wel B, Leaney R (2000) Assessing the impacts of dryland salinity on South Australia's water resources. 9/00, CSIRO Land and Water, Adelaide
- Jolly I, Williamson DR, Gilfedder M, Walker GR, Morton R, Robinson G, Jones H, Zhang L, Dowling TI, Dyce P, Nathan RJ, Nandakumar N, Clarke R, McNeill V (2001) Historical stream salinity trends and catchment salt balances in the Murray-Darling Basin, Australia. Mar Freshw Res 52:53–63
- Jones BF, Hanor JS, Evans WR (1994) Sources of dissolved salts in the central Murray Basin, Australia. Chem Geol 111: 135–154
- Kayaalp AS (2001) Application of rainfall chemistry and isotope data to hydro-meteorological modelling. PhD Thesis, The Flinders University of South Australia, Adelaide

- Lyne V, Hollick M (1979) Stochastic time-variable rainfall-runoff modelling. I.E. Australia National Conference Publication No. 79/10, Institute of Engineers Australia, Canberra
- Milnes AR, Bourman RP, Fitzpatrick RW (1987) Petrology and mineralogy of 'laterites' in southern and eastern Australia and southern Africa. Chem Geol 60:237–250
- Nathan RJ, McMahon TA (1990) Evaluation of automated techniques for base flow and recession analyses. Water Resour Res 26(7):1465–1473
- Pannewig MK (1992) Electromagnetic induction salinity surveys in a fractured rock system. BSc (Honours) Thesis, University of Adelaide, Adelaide
- Peck AJ, Hurle DH (1973) Chloride balance of some farmed and forested catchments in southwestern Australia. Water Resour Res 9(3):648–657
- Primary Industries and Resources of South Australia (PIRSA) 2002. Water Quality monitoring at Brukunga. EPA Licence No 10577, Condition 100-2. Regulation and Rehabilitation Unit Mineral Resources Group. Office of Minerals & Energy Resources, PIRSA, Adelaide, pp 72
- Radke BM, Watkins BM, Ivkovic KW, Cresswell RG, Bauld J (2000) A Groundwater Quality Assessment of the Upper Onkaparinga Region, Southern Mt Lofty Ranges, South Australia. Bureau of Rural Sciences, ACT, Canberra

- Salama RB, Farrington P, Bartle GA, Watson GD (1993) The chemical evolution of ground water in a first-order catchment and the process of salt accumulation in the soil profile. J Hydrol 143:233–258
- Schofield NJ, Ruprecht JK (1989) Regional analysis of stream salinization in southwest Western Australia. J Hydrol 112:19–39
- Smitt C, Herczeg A, Davies P, Cox J (2004) Identifying sources of salt and its mobilization processes in the eastern Mt Lofty Ranges, South Australia, Conference Proceedings: The 9th Murray-Darling Basin Ground water Workshop, Bendigo, February 2004
- Walker G, Cox J, Wilford J, Smitt C (2004) South Australian salt mapping and salinity management support program Bremer Hills site. Final report. CSIRO Land and Water Client Report, CISRO, Clayton, South VIC, pp 18
 Williamson DR, van der Wel B (1991) Quantification of the impact
- Williamson DR, van der Wel B (1991) Quantification of the impact of dryland salinity on water resources in the Mt Lofty Ranges, SA, Proceedings of the International Hydrology and Water Resources Symposium. The Institution of Engineers Australia National Conference Publication No. 91/22, Institution of Engineers Australia, Perth, pp 48–52
- Williamson DR, Stokes RA, Ruprecht JK (1987) Response of input and output of water and chloride to clearing for agriculture. J Hydrol 94:1–28