Chemical Geology 357 (2013) 164–177

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Geochemical and hydrological processes controlling groundwater salinity of a large inland wetland of northwest Australia

Grzegorz Skrzypek [a,b,*], Shawan Dogramaci [b,c], Pauline F. Grierson [a,b]

[a] West Australian Biogeochemistry Centre, School of Plant Biology, The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia
[b] Ecosystems Research Group, School of Plant Biology, The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia
[c] Rio Tinto Iron Ore, 152-158 St George's Terrace, Perth, WA 6000, Australia

ARTICLE INFO

Article history:
Received 30 January 2013
Received in revised form 19 August 2013
Accepted 21 August 2013
Available online 29 August 2013

Editor: David R. Hilton

Keywords:
Fortescue Marsh
Pilbara
Salinity
Groundwater
Stable isotopes
Cl/Br

ABSTRACT

Understanding mechanisms of hydrochemical evolution of groundwater under saline and brine wetlands in arid and semiarid regions is necessary to assess how groundwater extraction or injection in large-scale basins may affect the natural interface between saline–fresh aquifers in those systems. We investigated the evolution of groundwater of the Fortescue Marsh, a large inland wetland of northwest Australia that is mainly supplied by floodwater from the upper Fortescue River catchment. The marsh is located in the Pilbara region, one of the world's major iron ore provinces, where mining activities often occur below water tables. Here, we quantified the stable isotope and chemical composition of groundwater, surface water and rainfall in and around the marsh to better understand how saline marshes and playa lakes function geochemically, hydrologically and ecologically. The deep groundwater (>50 m depth) of the Fortescue Marsh is highly saline (>100 g L^{-1}), whilst shallow groundwater (~0–20 m depth) and surface water are mainly fresh or brackish. Currently, the marsh is mainly recharged by occasional floodwater. Consequently, salt in the marsh is concentrated by evaporation of rainfall. We expected that the hydrochemical composition of surface and groundwater would therefore reflect the chemical composition of rainwater. We analysed 206 water samples for stable isotope composition (δ^2H, δ^{18}O) and water chemistry, including: pH, dissolved oxygen, electrical conductivity (EC), and total dissolved solids (TDS), as well as Na, Ca, Mg, K, Si, Fe, HCO_3, SO_4, Cl, Sr and Br. We then developed geochemical models and a salt inventory to estimate the geological time of salt accumulation and to decouple geochemical characteristics of salt from modern groundwater. We found that groundwater associated with the marsh can be divided into two distinct groups that are characterised by their stable isotope compositions; i) fresh and brackish groundwater (TDS <10 g L^{-1}; δ^{18}O -8.0 ± 0.9‰) and ii) saline and brine groundwater (TDS >10 g L^{-1}, δ^{18}O varies from +2.5 to −7.2‰). Fresh groundwater was evaporated by <20% compared to rainwater. Brackish water mainly reflects modern recharge whilst saline and brine groundwater reflects mixing between modern rainfall, brackish water and relatively old groundwater. The Cl load in the groundwater originates from rainfall and accumulates over time as it is recycled due to precipitation of evaporates and re-dissolution on the marsh during subsequent flooding events. The stable isotope composition of the deeper brine groundwater also suggests a complex evolution, which cannot be explained by evaporation under current conditions from modern rainfall. We thus conclude that the deeper brine groundwater under the Fortescue Marsh developed under a different climatic regime and that the current salt in the marsh has accumulated over at least 40,000 years, but could have been as long as 700,000 years.

1. Introduction

Wetland environments, including inland salt lakes and marshes, are important ecological systems, serving as specialist habitats that also store and filter water and dampen flood and storm effects. Wetlands are driven by their hydrologic regimes, which can be extreme in warm, arid environments as they are often subject to prolonged droughts interrupted by episodic rainfall events. In particular, wetlands in arid regions are susceptible to chemical transformations of their shallow groundwater in drought periods through hypersalinity or through mobilisation of metals and acidification associated with redox changes. Whilst there has been

* Corresponding author at: School of Plant Biology M090, The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia. Tel.: +61 8 6488 4584.
E-mail addresses: grzegorz.skrzypek@uwa.edu.au, gskrzypek@yahoo.com (G. Skrzypek), shawan.dogramaci@riotinto.com (S. Dogramaci), pauline.grierson@uwa.edu.au (P.F. Grierson).

0009-2541
http://dx.doi.org/10.1016/j.chemgeo.2013.08.035

increasing attention given to surface water–groundwater interactions across a range of ecosystem types, particularly with respect to water fluxes, biogeochemical processes and ecology, the groundwater isotope geochemistry of inland wetland systems in more arid regions remains poorly understood (Lamontagne et al., 2005; Jolly et al., 2008).

Saline wetlands and lakes are common in the arid regions of inland Australia, where evaporation can greatly exceed rainfall. These saline ecosystems are usually formed in internally drained basins whenever the floors of such basins intersect the water table (Duffy and Al-Hassan, 1988; Yechiechi and Wood, 2002). The salinity of inland lakes is mainly driven by either evaporation of slowly discharging groundwater (groundwater dependent lakes), or progressive evaporation of rapidly delivered pulses of floodwaters that eventually seeps and mixes with the underlying groundwater (surface water dependent lakes). Most of the inland saline lakes and marshes across Australia are of the former type and considered “windows” to underlying highly evaporated groundwater (Rosen et al., 1994; Harrington et al., 2008). In such systems, the hydrochemistry of the lake water is mainly dependent on the degree of evaporation and on the mineralogy and chemical composition of the rocks through which the groundwater percolates. Generally, groundwater becomes more saline with increasing distance from recharge zones, where time for water–rock interaction is longer, resulting in aquifer mineral dissolution and exchange with groundwater in the discharge zones (Chebotarev, 1955). In groundwater fed systems, the discharge is also assumed to be relatively constant over time and frequently concentrations of major ions are close to saturation.

In contrast to these saline playa lake systems, large-scale wetlands mainly supplied by occasional floodwater are relatively uncommon in Australia's inland. Salt in these wetlands originates from evaporation of rainfall; surface and groundwater hydrochemical compositions are thus likely to reflect the chemical composition of rainwater inputs (Herczeg and Edmunds, 1999). Large volumes of fresh floodwater are delivered sporadically (on cycles of years to decades), such that the wetland is subject to rapid wetting periods when floodwater is rushing in to a terminal basin followed by a slow drying period as the water progressively evaporates. As a consequence, the salinity of the surface water varies over time as initially delivered water is fresh and becomes progressively more saline as it evaporates. In both types of systems, extensive evaporation often leads to accumulation of carbonates, gypsum and halite (Rosen et al., 1994; Harrington et al., 2008; Cartwright et al., 2010). Precipitation of calcium and magnesium carbonates can also result in formation of thick layers of calcrete, which in turn act as a “hard pan”, restricting surface water infiltration and mixing of surface water with groundwater. However, the relative influence of these differing mechanisms of groundwater evolution on the natural interface between saline–fresh aquifers in these systems is not clear.

Geochemical modelling and quantification of the stable isotope and chemical composition of groundwater, surface water and rainfall may help in understanding how saline marshes and playa lakes of these types function hydrologically (and therefore ecologically) and what hydrochemical and hydrological regimes are responsible for their formation. A combination of stable isotope and biogeochemical analyses is particularly useful for determining evaporative losses and time of water retention in surface pools (Fellman et al., 2011), characterisation of local recharge conditions and unravelling reasons for increasing groundwater salinity (Tweed et al., 2011; Costelloe et al., 2012), as well as for calculation of the volume of rain required to induce recharge in arid zones (Harrington et al., 2002; Dogramaci et al., 2012). The chemical and stable isotope composition of groundwater can also be used to identify the dominant hydrological processes in semiarid basins and present day relationships between their hydrology and water chemistry (Acheampong and Hess, 2000; Herczeg et al., 2001; Harrington et al., 2008).

Stable isotopic mass balance models have also been successfully utilised in studies of various saline lake complexes (Herczeg et al., 1992; Gat and Levy, 1978). In addition, untangling processes that involve groundwater–surface water interactions requires understanding of the effects of topography, geology and climate on groundwater flow regimes (Toth, 1963). This multidimensional approach allows reconstruction of geochemical processes leading to formation of saline and brine terminal lakes that are frequently associated with unique saline ecosystems (Bowler, 1986; Dutkiewicz et al., 2000; Yechiechi and Wood, 2002).

The Fortescue Marsh is the largest wetland of inland northwest Australia; however, the extent of surface water on the marsh varies dramatically from total dryness to >1000 km^2 depending on the frequency and intensity of rainfall. The marsh receives drainage from the upper catchment of the Fortescue River in the Hamersley Basin. The Lower Fortescue River is separated from the Fortescue Marsh and Upper Fortescue River by the Goodiadarrie Hills (Fig. 1A, B). Surface water overflow may occur only after very large cyclones, events that may occur only a few times every 100 years. Unlike surface water flow, groundwater horizontal flow is very slow and hydraulic conductivity ranges from 0.1 to 1 m/day (Rio Tinto, 2013). The degree to which there is groundwater discharge from the Fortescue Marsh to the Lower Fortescue River is currently unknown, although discharge, if any, is likely to be very slow given the horizontal flow rates across the marsh.

The deep groundwater (>50 m b.g.l, below ground level) of the Fortescue Marsh is highly saline (>100 g L^{-1}), whilst shallow waters and surface water are fresh or brackish. This contrasts with the majority of saline wetlands and playa like systems in Australia, which are characterised by higher salinity in the shallow aquifers due to direct evaporation from exposed groundwater or through capillary action (De Dekker, 1988). Thus, the Fortescue Marsh is acting at least in part as a terminal basin recharged via episodic cyclones coupled with frequent and prolonged dry periods. This unusual combination has led to unique hydrochemical characteristics and relationships between fresh and saline waters.

Understanding the evolution of surface and groundwater hydrochemistry, especially the balance between highly saline and fresh groundwater, is crucial for proper water management in arid zones in the face of both anthropogenic and climate driven changes. The Fortescue Marsh, similar to many arid zone wetlands around the world, is an area of high national and international conservation significance (Environmental Protection Authority, 2013). The marsh is also located in one of the world's major iron ore provinces; ore extraction has undergone rapid expansion in recent decades and mining activities often occur below water tables, which require new strategies and new knowledge for optimising water management (Environmental Protection Authority, 2013). Rainfall across the Pilbara region over recent decades has also been high relative to the preceding century or so (Cullen and Grierson, 2007), although future climate scenarios and the frequency of recharge events resulting from summer cyclones remain uncertain. Consequently, there is an urgent need to better understand the hydrologic functioning of key systems in order to assess the risk and potential impacts of changing hydrological regimes on groundwater resources across the region.

Here, we sought to understand groundwater flow regimes and to determine the predominant processes that contribute to the water and salt balance and evolution of hydrochemistry in the Fortescue Marsh catchment. We used a conventional mass balance model based on major ions, geochemical modelling as well as water stable isotopes (δ^2H and δ^{18}O), to distinguish the sources of water and salt in various geochemical types of water. We also estimated the time required for salt accumulation in the Fortescue Marsh and propose a model to explain how salt beneath the marsh accumulates and why brackish waters have stable isotope signatures similar to that of fresh waters.

2. Materials and methods

2.1. Hydrology and hydrogeology of the Fortescue Valley

The Fortescue Marsh occupies a trough between the Chichester and Hamersley ranges in the semi-arid Pilbara region of northwest Australia