Chemical Geology 251 (2008) 77–98

Contents lists available at ScienceDirect

Chemical Geology

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

Coupling mineral analysis with conceptual groundwater flow modelling: The source and fate of iron, aluminium and manganese in a back-barrier island

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ARTICLE INFO

Article history:
Received 1 June 2007
Received in revised form 26 February 2008
Accepted 26 February 2008

Editor: J. Fein

Keywords:
Iron oxide–hydroxides
Density dependent flow
Baroclinic
Barotropic
Redox couples

ABSTRACT

Mineral and aqueous geochemical data are combined with a conceptual groundwater flow model, to establish the origin and fate of iron, aluminium and manganese in the groundwater system of a small back-barrier island. The flow model domain consists of an unconfined island fresh groundwater lens overlying a semi-confined hypersaline aquifer. The two aquifers are separated by a discontinuous, clay-rich aquitard and both contain diffusion governed variable density flow fields. High concentrations of dissolved iron and manganese are associated with brackish to hypersaline groundwater, although there is no systematic relationship with salinity. Calculation of S^{2-}/SO_4^{2-} and Fe^{2+}/Fe^{3+} redox couples and the results of thermodynamic modelling show that redox disequilibrium in the groundwater is widespread. Groundwater samples containing aqueous sulphide and ferric iron complexes are supersaturated with respect to pyrite, goethite and haematite but the prevailing state of redox disequilibrium controls mineral dissolution and precipitation. Aqueous iron in the deeper regions of both aquifers is derived from the dissolution of iron oxide–hydroxides in lateritic palaeosols controlled by seasonal fluctuations in groundwater redox state. Aqueous manganese is potentially derived from the dissolution of ilmenite and amorphous oxide–hydroxides. The oxidation of iron sulphides contributes to the aqueous iron concentration and sulphuric acid production in the shallow groundwater. The solubility of aluminium is also limited by this process, governed by acidity regulation. A significant proportion of aqueous iron is transmitted from the semi-confined to the overlying unconfined aquifer through discontinuities in the aquitard layer. Movement of metals in solution outside the island groundwater system is restricted by the presence of diffusion boundaries within variable density transition zones.

1. Introduction

Secondary iron- and aluminium-bearing minerals are ubiquitous products of sub-aerial weathering in siliciclastic sediments (Drever, 1997; Cornell and Schwertmann, 2003). Coastal zone environments host a wide range of both mineral groups, as detrital grains and secondary alteration products. The suite of stable secondary minerals produced is governed by climatic conditions, the drainage characteristics of the sedimentary pile and pore-water composition (Tardy et al., 1973; Ingles and Ramos-Guerrero, 1995; Ahlberg et al., 2003; Preda and Cox, 2004; Liaghati et al., 2005b).

Small back-barrier islands are a common geomorphic feature in estuaries globally due to the Holocene high-stand and the subsequent fall in relative sea-levels. The very low topographic elevations of these landforms and their close proximity to the shoreline promote the development of complex multi-aquifer groundwater systems (Hodgkinson et al., 2007). All island aquifers host a fresh groundwater lens (Collins and Easley, 1999; Robins and Lawrence, 2000), but unlike large barrier islands or isolated atolls the freshwater lens in a back-barrier island may interact with mainland aquifers, particularly when associated with buried palaeovalleys. Until recently these small islands have received little attention and have been overlooked as discrete hydrogeological entities (Hodgkinson et al., 2007, 2008).

Coastal groundwater studies have examined the relationship between sediment geochemistry and seasonal fluxes (e.g. Preda and Cox, 2000; Liaghati et al., 2004) but most coastal groundwater research has focused on flow behaviour and solute transport related to salt water intrusion (e.g. Li and Jiao, 2003; Werner and Lockington, 2004; Robinson et al., 2006) or water–rock interaction related to specific minerals of interest (Alvarez et al., 2005; Peacock and Sherman, 2005; Beig and Luttge, 2006; Nowack and Stone, 2006). Island hydrogeological studies have primarily concentrated on freshwater lens geometry and dynamics (e.g. Collins and Easley, 1999; Ritzi et al., 2001; Schneider and Kruse, 2005) or groundwater resource

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0009-2541/$ – see front matter
doi:10.1016/j.chemgeo.2008.02.017

potential (Harbison and Cox, 1998; Werner and Williams, 1999; Armstrong, 2006). A holistic approach incorporating all of these factors in an island setting has not been used to date.

This study provides new insights into the complexity of back-barrier island groundwater systems and the importance of understanding their significance as discrete hydrogeological entities in regional estuarine groundwater systems. A conceptual groundwater flow model is combined with hydrochemistry, sediment mineralogy and a thermodynamic framework for mineral solubility. The interdisciplinary approach is applied to constrain the source to sink behaviour of iron, manganese and aluminium. The interaction between a thinned island freshwater lens and an underlying palaeovalley-hosted aquifer and the effects on solute transport are determined.

2. Geology and hydrogeology

Toorbul Island is a low-lying back-barrier sand island, located in the Pumicestone Passage on the east coast of Queensland, Australia (Fig. 1). The passage forms a shore-parallel estuarine tidal lagoon behind the large Bribie Island sand barrier to the east (Harbison and Cox, 1998; Lang et al., 1998; Armstrong and Cox, 2002). Maximum topographic elevation on Toorbul Island is 3.5 m AHD, with an average of ~1.5 m AHD and a total surface area of ~5 km^2. The island consists of an unconsolidated sedimentary pile ~6 m to 24 m thick (Fig. 2), unconformably overlying pervasively weathered, largely impermeable, sandstone bedrock (Hodgkinson et al., 2006, 2008), which has been cited as a major source of iron (Preda and Cox, 2002; Liaghati et al., 2005a).

A shallow, bedrock incised palaeovalley passes beneath Toorbul Island and the unconsolidated valley-fill sediments form one of two aquifers that constitute the groundwater system (Figs. 2 and 3). The deeper aquifer is semi-confined by a thin (<2 m), discontinuous, Quaternary palaeosol (Hodgkinson et al., 2006, 2008). Shoreface and estuarine sediments overlie the palaeosol and were deposited as part of the large progradational chenier plain complex of Bribie Island (Lang et al., 1998). This sedimentary unit forms the bulk of the overlying unconfined aquifer on Toorbul Island (Hodgkinson et al., 2008).

The Toorbul Island aquifers are divided into baroclinic and barotropic fields (Fig. 4) (Hodgkinson et al., 2007). Fluid density in a baroclinic field varies laterally, whereas lateral density is constant in a barotropic field (Neuman and Pierson, 1966; Hickey, 1989). The unconfined aquifer exhibits landward dipping brackish transition zones, characteristic of higher density intruding saline seawater wedges in coastal environments (Fig. 4). The deeper semi-confined aquifer hosts hypersaline groundwater and exhibits the opposite transition zone geometry, dipping seaward, due to the reverse in

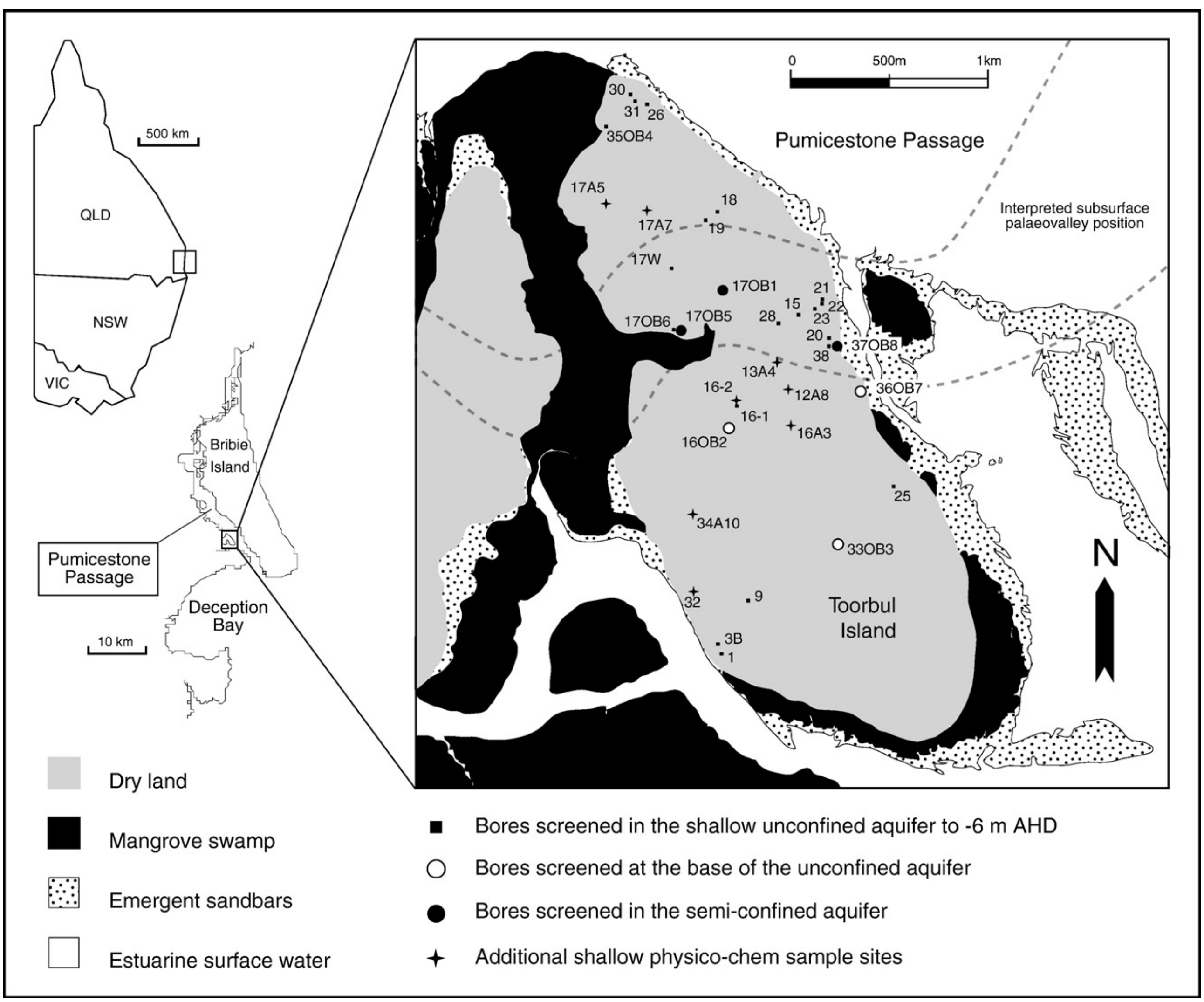

Fig. 1. Study area location map and sample sites.