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Research papers

Model-based analysis of δ^{34}S signatures to trace sedimentary pyrite oxidation during managed aquifer recharge in a heterogeneous aquifer

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ABSTRACT

The oxidation of pyrite is often one of the main drivers affecting groundwater quality during managed aquifer recharge in deep aquifers. Data and techniques that allow detailed identification and quantification of pyrite oxidation are therefore crucial for assessing and predicting the adverse water quality changes that may be associated with this process. In this study, we explore the benefits of combining stable sulphur isotope analysis with reactive transport modelling to improve the identification and characterisation of pyrite oxidation during an aquifer storage and recovery experiment in a chemically and physically heterogeneous aquifer. We characterise the stable sulphur isotope signal (δ^{34}S) in both the ambient groundwater and the injectant as well as its spatial distribution within the sedimentary sulphur species. The identified stable sulphur isotope signal for pyrite was found to vary between −32 and +34‰, while the signal of the injectant ranged between +9.06 and +14.45‰ during the injection phase of the experiment. Both isotope and hydrochemical data together suggest a substantial contribution of pyrite oxidation to the observed, temporally variable δ^{34}S signals. The variability of the δ^{34}S signal in pyrite and the injectant were both found to complicate the analysis of the stable isotope data. However, the incorporation of the data into a numerical modelling approach allowed to successfully employ the δ^{34}S signatures as a valuable additional constraint for identifying and quantifying the contribution of pyrite oxidation to the redox transformations that occur in response to the injection of oxygenated water.

1. Introduction

Excess surface water captured during wet seasons is often stored in open dam lakes (e.g., Graf, 1999; Altinbilek, 2002). However, the retained water is subject to substantial evaporative losses, particularly in warm and dry climates. Underground storage through managed aquifer recharge (MAR) can protect the resource from these losses and provide a valuable water management tool in water stressed regions (Dillon, 2005). One of the major challenges for MAR is the potential deterioration of the water quality that is induced by the geochemical reactions between the often oxygenated injectant and the aquifer matrix (Maliva et al., 2006). Especially in deep aquifers, the oxidation of pyrite is in many cases the key process that drives undesired modifications of the injectant water quality during subsurface passage and storage (e.g., Stuyfzand, 1998; Saaltink et al., 2003; Prommer and Stuyfzand, 2005; Jones and Pichler, 2007; Descourvieres et al., 2010a,b; Wallis et al., 2010). Depending on the site-specific aquifer geochemistry and the hydrochemical composition of the injectant these modifications can adversely impact the groundwater quality to the extent that the water becomes unsuitable for the intended use (e.g., Jones and Pichler, 2007; Neil et al., 2014). Most importantly the interactions between the typically oxygenated or nitrate containing injectant and pyrite have often been shown to strongly affect the redox zonation of the target aquifer (Stuyfzand, 1998; Prommer and Stuyfzand, 2005; Wallis et al., 2010, 2011; Antoniou et al., 2012, 2013; Seibert et al., 2016). This directly influences the removal potential of micropollutants (e.g., pharmaceuticals, personal care products, disinfection by-products and iodated contrast media) that may prevail in the injectant at residual concentrations and often degrade preferentially under specific redox conditions (Greskowiak et al., 2006; Pavelic et al., 2006; Carrara

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et al., 2008; Barbieri et al., 2011; Maeng et al., 2011; Burke et al., 2014a,b; Henzler et al., 2014). On the other hand, pyrite oxidation also increases the risk of groundwater quality deterioration through the release of metals and metalloids such as arsenic (Jones and Pichler, 2007; Descourvieres et al., 2010a; Wallis et al., 2010, 2011; Neil et al., 2014), and through groundwater acidification, which facilitates the mobility of heavy metals where the aquifer's matrix buffering capacity is low (Kjøller et al., 2004; Descourvieres et al., 2010a). A detailed characterisation and investigation of the factors affecting pyrite oxidation is therefore crucial to reliably identify and predict geochemical reactions and the associated long term water quality evolution that occur in response to managed aquifer recharge.

Over the past few decades, stable sulphur isotope analysis (SSIA) has been established as a powerful tool for tracing pyrite oxidation and other sulphur cycling processes in various environments (e.g., Strebel et al., 1990; Eckert and Appelo, 2002; Massmann et al., 2003; Herczeg et al., 2004; Le Gal La Salle et al., 2005; Donahue et al., 2008; Schwientek et al., 2008; Dale et al., 2009; Otero et al., 2009; Prommer et al., 2009; Gibson et al., 2011; Zhang et al., 2012, 2013). The method relies on the typically large differences in the stable sulphur isotope ($\delta^{34}S$) signals between the reduced and the oxidised sulphur species (e.g., Strebel et al., 1990; Bottrell et al., 1995; Spence et al., 2001; Trettin et al., 2002; Massmann et al., 2003; Schwientek et al., 2008; Gibson et al., 2011). This characteristic difference is caused by isotope fractionation processes that occur during bacterial sulphate reduction, the predecessor for sedimentary pyrite formation, which results in a significant depletion in ^{34}S for the produced sulphide against the original sulphate source (Kaplan and Rittenberg, 1964; Rees, 1973; Chambers and Trudinger, 1979; Canfield, 2001; Brunner and Bernasconi, 2005). The ^{34}S depleted signal is subsequently captured during the formation of sedimentary pyrite and preserved (Böttcher et al., 1998). However, at a later stage it may be (i) released back to the groundwater with no or negligible fractionation (Balci et al., 2007) upon the intrusion of more oxidised waters that induce pyrite oxidation, and (ii) subsequently transported within the aquifer with no or only negligible additional fractionation (van Stempvoort et al., 1990).

In groundwater systems, previous studies have used SSIA to prove pyrite oxidation and bacterial sulphate reduction during deep-well managed aquifer recharge in a carbonate aquifer (Herczeg et al., 2004; Le Gal La Salle et al., 2005), to identify major sources and governing processes for sulphate concentrations during acid mine drainage (Taylor et al., 1984; Edraki et al., 2005), and to constrain the consumption of aqueous nitrate through sulphide oxidation for aquifers polluted by high nitrate concentration (Schwientek et al., 2008; Otero et al., 2009; Zhang et al., 2012, 2013). Other applications used SSIA to estimate the extent of sulphate reduction over the isotopic enrichment of residual sulphate in the context of natural attenuation of oxidisable organic or emerging metal contaminants (Lee and Saunders, 2003; Knöller et al., 2008; Prommer et al., 2009; Gibson et al., 2011), to identify competing processes during enhanced remediation of hydrocarbons (Eckert and Appelo, 2002), and to investigate marine and biogenic sulphur cycling (Wijsman et al., 2001; Donahue et al., 2008; Skrzypek et al., 2008; Dale et al., 2009).

The detailed interpretation of sulphur stable isotope data collected under field conditions requires the consideration of complex hydrogeological and hydrochemical processes that may affect the isotope signal during subsurface passage and thus relies strongly on capturing the aquifer's physical and chemical heterogeneity (e.g., Knöller et al., 2008). In the case of stable carbon isotope signatures, and to a lesser extent for nitrogen isotopes, reactive transport modelling has been shown to assist with the integrative analysis of the interacting physical and geochemical processes that control these isotope signatures in heterogeneous aquifer systems (e.g., van Breukelen and Prommer, 2008; Pooley et al., 2009; D'Affonseca et al., 2011; Höyng et al., 2015; Rodríguez-Escales et al., 2014, 2016). However, only a few studies have considered the value of field scale numerical modelling of $\delta^{34}S$ signatures and their potential contribution to exploring heterogeneous and transient conditions (Eckert and Appelo, 2002; Prommer et al., 2009; Zhang et al., 2013). The field studies by Eckert and Appelo (2002) and Zhang et al. (2013) that analyse pyrite oxidation report either a narrow $\delta^{34}S$ signal range (−21 to −16‰) or assign a single $\delta^{34}S$ value (−4.2‰) for sedimentary pyrite. However, studies by Wijsman et al. (2001) and Ferrini et al. (2010) have shown that in some sedimentary units the $\delta^{34}S$ signal of pyrite may vary up to ±50‰ even over very small distances, depending on various diagenetic or syn-depositional influences. Such large variabilities of the $\delta^{34}S$ signal in pyrite are likely to occur especially in heterogeneous aquifers and are thought to add additional complexity to the application of SSIA.

In this study we explore the potential benefits of employing SSIA for the enhanced characterisation of pyrite oxidation processes during a large scale aquifer storage and recovery (ASR) experiment in a chemically and physically heterogeneous aquifer near Perth, Western Australia. The well controlled ASR experiment provides an ideal field laboratory for the examination of a heterogeneous aquifer and the field site as well as most site relevant processes have been extensively characterised by previous studies (Descourvieres et al., 2010a, 2010b, 2011; Descourvieres, 2011). The aims of this study are (i) to characterise the stable sulphur isotope signal with respect to its vertical distribution and variations within a strongly heterogeneous aquifer, and (ii) to examine the feasibility of using SSIA in combination with reactive transport modelling as a supporting tool for the identification and improved quantification of pyrite oxidation.

2. Materials and methods

2.1. Study site

The research at the study site was aimed to investigate the technical feasibility of ASR operations in the Perth Basin as a mean to mitigate seasonal water supply imbalances of the Perth Metropolitan area. The trial site (referred to as M345) was located approximately 15 km North of Perth and consisted of an ASR injection/recovery well and five monitoring wells (M01/08, M02/08, M03/08, M04/08 and M01/09) installed 15–40 m from the ASR well (Fig. 1). The injection horizon stretched over a total depth of 105 m between 320 and 425 meters below ground level (m bgl) and comprised two injection intervals (320–370 m bgl and 395–425 m bgl) separated by a 25 m section of blank casing. The 6–9 m long screens of the monitoring wells were located at variable depths within the injection intervals (Fig. 2). Due to operational problems, groundwater monitoring well M01/09 was only used to obtain the initial groundwater chemistry.

The targeted aquifer is a part of the Cretaceous Leederville Formation and consists predominantly of poorly consolidated sandstones with interbedded siltstones and mudstone/shale layers of marine and continental origin (Davidson, 1995; Descourvieres et al., 2010a, 2011; Leyland, 2011). At the injection site, the main aquifer encompasses the Wanneroo Member (250–515 m bgl) of the Leederville Formation. It is locally confined by alternating siltstones, silty sandstones and shales of the Pinjar and Mariginiup Member at the aquifer top and bottom respectively (Descourvieres et al., 2010a; Descourvieres, 2011). The aquifer is strongly stratified but had relatively homogeneous horizontal permeabilities within the vicinity of the injection zone.