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Reactive transport impacts on recovered freshwater quality during multiple partially penetrating wells (MPPW-)ASR in a brackish heterogeneous aquifer

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ABSTRACT

The use of multiple partially penetrating wells (MPPW) during aquifer storage and recovery (ASR) in brackish aquifers can significantly improve the recovery efficiency (RE) of unmixed injected water. The water quality changes by reactive transport processes in a field MPPW-ASR system and their impact on RE were analyzed. The oxic freshwater injected in the deepest of four wells was continuously enriched with sodium (Na^+) and other dominant cations from the brackish groundwater due to cation exchange by repeating cycles of 'freshening'. During recovery periods, the breakthrough of Na^+ was retarded in the deeper and central parts of the aquifer by 'salinization'. Cation exchange can therefore either increase or decrease the RE of MPPW-ASR compared to the RE based on conservative Cl^-, depending on the maximum limits set for Na^+, the aquifer's cation exchange capacity, and the native groundwater and injected water composition. Dissolution of Fe and Mn-containing carbonates was stimulated by acidifying oxidation reactions, involving adsorbed Fe^{2+} and Mn^{2+} and pyrite in the pyrite-rich deeper aquifer sections. Fe^{2+} and Mn^{2+} remained mobile in anoxic water upon approaching the recovery proximal zone, where Fe^{2+} precipitated via MnO_2 reduction, resulting in a dominating Mn^{2+} contamination. Recovery of Mn^{2+} and Fe^{2+} was counteracted by frequent injections of oxygen-rich water via the recovering well to form Fe and Mn-precipitates and increase sorption. The MPPW-ASR strategy exposes a much larger part of the injected water to the deeper geochemical units first, which may therefore control the mobilization of undesired elements during MPPW-ASR, rather than the average geochemical composition of the target aquifer.

1. Introduction

Aquifer storage and recovery (ASR) using wells can be a successful freshwater management tool in coastal areas worldwide by keeping temporary freshwater surpluses available for periods of shortage (Pyne, 2005). Freshwater surpluses are stored this way for later use in times of demand, creating a self-sufficient freshwater supply which makes external freshwater supply (including infrastructure) and/or costly desalination superfluous. However, application of especially small-scale ASR systems in aquifers with brackish or saline groundwater often results in a low recovery efficiency (RE: part of the injected water that can be recovered with a satisfying quality) due to buoyancy effects (Ward et al., 2009; Zuurbier et al., 2013). Also, the buoyancy effects may preclude a progressively improving water quality with subsequent cycles as observed at conventional ASR systems (Ward et al., 2009). Recently, the use of multiple partially penetrating wells (MPPW) installed in a single borehole in a brackish aquifer allowed significantly higher recovery efficiencies by deep injection and shallow recovery, as demonstrated for relatively unmixed rainwater containing <0.5 mmol/l Na^+ (Zuurbier et al., 2014). While that study focused on the buoyancy and mixing effects on the conservative transport of chloride (Cl^-), other water quality parameters may determine the final success of ASR, depending on the intended use. Sodium (Na^+), for example, may threaten the water quality for irrigation since it is toxic in low concentrations for various plants or crops (Kronzucker and Britto, 2011), but also for drinking and industrial purposes. Also, arsenic is known to be toxic for both humans and plants (National Research Council, 1977). Besides toxic effects, operational aspects, such as the clogging of pumps, pipelines, and

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sprinklers by the precipitation of manganese or iron oxides, may determine the suitability of the recovered water for direct use(-Pyne, 2005). Especially for agricultural end users, recovered water upon aquifer storage ought to be directly usable to limit the water costs. Although the elements of concern are typically low in ASR ‘injection water’ (i.e. the water that is to be injected, after which it becomes ‘injected water’), enrichment may occur by freshening and salinization (e.g., Appelo, 1994a, 1994b; Stuyfzand, 1993; Valocchi et al., 1981) and dissolution of carbonates (Antoniou et al., 2012; Stuyfzand, 1998). Additionally, the injection of oxygen and/or nitrate-containing water in a deeply anoxic target aquifer may induce mobilization of SO_4, Fe, Mn, and As, which has been reported in ASR studies worldwide (e.g., Antoniou et al., 2012; Jones and Pichler, 2007; Neil et al., 2014; Price and Pichler, 2006; Stuyfzand, 1998; Vanderzalm et al., 2011; Wallis et al., 2010, 2011).

The operation of an MPPW-ASR system does not comply with the more traditional ASR-theories for bi-directional horizontal flow directions during injection and recovery via fully penetrating well screens in aquifers without significant buoyancy effects. During MPPW-ASR, instead, (oxygen-rich) freshwater is predominantly injected in brackish aquifers via the deeper wells while extraction occurs at shallower wells. Consequently, vertical transport exposes the injected water to a vertical range of geochemical heterogeneities in the aquifer and the associated potential sources of water quality deterioration. Additionally, hydrochemical conditions at the deeper wells are highly dynamic, with frequent alternations of freshening (during injection) and salinization (during storage/recovery). In this study, therefore, we analyzed the observed water quality changes by reactive transport processes in a field MPPW-ASR system with a focus on cation-exchange and redox-reactions and their impact on the RE. Hydrochemical data were collected during the field MPPW-ASR pilot in a brackish aquifer for which Zuurbier et al. (2014) described the hydrological aspects and freshwater recoverability based on *conservative transport* (chloride). The aim of this study was to assess for the same MPPW-ASR system how *reactive transport* processes affected the concentrations of Na^+, Fe^{2+}, Mn^{2+}, and As in the recovered water over time. This provides a more complete analysis of the application and operational optimization of MPPW-ASR systems.

2. Materials and methods

The application of an MPPW-ASR system in a brackish aquifer was well-monitored in a field pilot in 2012 and 2013 allowing to closely analyze the water quality development in the aquifer until recovery. This field pilot was preceded by a detailed physical and geochemical characterization of the aquifer to understand the flow patterns and water quality changes.

2.1. ASR field site

The Nootdorp MPPW-ASR system was built in 2011 with the aim to store rainwater collected by the roof of a 20,000 m^2 greenhouse, and to recover this water for irrigation purposes in the same greenhouse (more details in Zuurbier et al., 2014). The MPPW, with four independently operated well screens at distinct aquifer intervals installed in a single borehole, were used to maximize the freshwater recovery (Fig. 1). The ASR system was extensively monitored for this study from January 2012 until September 2013.

The unconsolidated target aquifer is confined by unconsolidated clay and peat. Geological characterization indicated that the target aquifer consists of middle-coarse to very coarse fluvial sands from the Rhine River (Zuurbier et al., 2014). The lower part (HU-f-i, Fig. 3) is a little coarser than the upper part (HU-a-c). A fine sand layer (HU-d) and a sand layer containing reworked clay and peat deposits in a coarse sand matrix (HU-e) are present in the middle of the target aquifer. This HU-e unit is dis-continuous and found only locally in the pilot area (Zuurbier et al., 2014). Besides local separation into two compartments by the clayey interval of this HU-e unit, the aquifer is relatively homogeneous, as indicated by geophysical and hydrochemical analysis during the first ASR cycle (Zuurbier et al., 2014).

2.2. Operation of the MPPW during the Nootdorp ASR pilot

The injection rate was equally distributed over all MPPW screens in the first 3 months (Fig. 2). From April 2012 until May 2013 only the lower three well screens (AWS2-4) were used for injection, while mainly the shallow AWS1 and AWS2 were used for recovery, accompanied by a low-rate recovery at AWS3 in Cycle 2. The freshwater surpluses in the last phase (Summer, 2013) were injected at AWS1-4 from May 2013 until August and at AWS1-S3 during the last month of the pilot. During the pilot phase, 39.9% (11,591 m^3) of the injected water (29,047 m^3) was abstracted.

2.3. Site characterization and hydrochemical monitoring

2.3.1. Physical and geochemical sediment analyses

To characterize the target aquifer and identify potentially reactive intervals 114 samples were taken from thin-wall tubes at intervals of 0.2 m or smaller whenever lithological variations appeared (Zuurbier et al., 2014), or from the bailer at the other intervals of MW1 (every meter, $n = 14$). Grain size distribution of each sample was determined using a laser particle sizer (Zuurbier et al., 2014). Hydrogeological units (HU-a to HU-h) and their hydraulic properties were derived using the grain size distributions, head responses at MW1 upon pumping, and the breakthrough curves of Cl^- at MW1 (Zuurbier et al., 2014). Sedimentary organic matter (SOM) and total carbonates were deduced from thermogravimetry (TGA at 330, 550, 1000 °C).

An XRF-core scan (Avaatech, The Netherlands) was executed on the cut cores for a semi-quantitative analysis of Al, S, Ca, Mn, and Fe on a split-core-surface area of 1 cm^2 over a time interval of 10 s using a generator setting of 10 kV. This way, reliable log-ratios of Fe/S, Fe/Ca, Mn/Ca, and S/Ca were obtained, which are linearly related to the log-ratios of quantitative element concentrations (Weltje and Tjallingii, 2008). Sediments samples were taken at 6 distinct depth intervals and sent for laboratory XRF to correct the log-ratios obtained by the high-resolution core-scan. The reader is referred to the Supplementary Information for more details on the log-ratio correlation derived. True elemental ratios were subsequently attained via these log-ratios and corrected for molal masses. S/Ca was used to derive the part of Fe/Ca that is related to pyrite, assuming $Fe = 0.5 \times S$. This way the potential relative presence of Ca, Fe, and Mn in the carbonates could be derived. In this approach the presence of these elements in silicates is neglected. Also the contribution of Mg to the carbonates is not considered, since this element is not measured by the XRF core-scan. For Fe/Al, an overestimation and a poor correlation was found with the laboratory analyses due to the relatively short measurement time of the core scan, insufficient to measure all Al present; it was therefore only used as a qualitative indication for the presence of reactive Fe (not bound to silicate minerals).

Geochemically similar units (GU-I to GU-V) were defined based on the high-resolution core-scan data. Per GU, 5 (GU-II, IV) or 10 (GU-I, II, V) equally distributed subsamples of approximately 30 g were taken from the core. Sampling depths were slightly adjusted only when equidistant sampling forced sampling of ‘unreliable intervals’, for instance by slumped sediment at the top 10 cm of each 1 m core. Each subsample was oven-dried and homogenized and then equally contributed (5 g or 10 g) to one mixed sample per GU (50 mg). These