Groundwater ages and reaction rates during seawater circulation in the Dead Sea aquifer

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Abstract

The Dead Sea system provides a unique opportunity to study flow velocities and reaction rates during seawater circulation in the aquifer. We present here a novel application of calculating groundwater age and velocity along the flow path of the hypersaline water from the Dead Sea into the aquifer using the buildup rate of ^{228}Ra in this water. The calculated circulation velocities are 1–10 m/y, which is in agreement with estimates based on the Na/Cl ratios in this water (1.5–4 m/y). The latter is unique to the Dead Sea-aquifer system, where the Na/Cl ratio has been decreasing during the past 50 years due to the precipitation of halite in the lake. The velocity estimates facilitated the calculation of the rates of water–rock interactions in the Dead Sea aquifer.

SO_4 is removed relatively fast ($k = 0.8$ y^{-1}) due to gypsum precipitation while barite or celestine precipitation removes ^{226}Ra and Ba in a time scale of years ($k = 0.22$ y^{-1}). Similar rates were found for redox-driven reactions, such as U removal ($k = 0.4$ y^{-1}) and Fe and Mn contribution due to the dissolution of oxides ($k = 0.15$ y^{-1}). In the fresh–saline groundwater transition zone, gypsum which precipitated from hypersaline water in higher lake stands, is now being dissolved and enrich the water with SO_4.

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1. INTRODUCTION

Seawater circulation in aquifers has been recently recognized as a major process in the mass balances of coastal areas (e.g. Simmons, 1992; Moore, 1996; Charette and Sholkovitz, 2006). The spatial and temporal scales of seawater circulation vary between the small-scale, short-term, such as wave- and tidal-driven (Robinson et al., 1998; Li et al., 1999) through seasonal scale (Michael et al., 2005) and up to the large-scale, long-term density-driven dispersive circulation (Cooper, 1959).

Unlike the short-term circulation, which was studied by several authors both through simulations and in the field (e.g. Li et al., 1999; Michael et al., 2005; Charette and Sholkovitz, 2006), the long-term dispersive circulation has been studied mainly by hydrological simulations (e.g. Lee and Cheng, 1974; Smith, 2004; Kiro et al., 2008), while it was hardly studied in the field (Kiro et al., 2012). Moreover, simulations of saline water circulation are very sensitive to the model parameters (e.g. dispersivities, anisotropy and permeability; Smith, 2004; Kiro et al., 2008), and therefore the simulation-calculated velocities should be cautiously treated.

The Dead Sea system provides a unique opportunity to study the long-term dispersive seawater circulation due to the absence of tides and significant waves and to the very shallow fresh–saline transition zone, which is the result of the extreme high density of the Dead Sea water.

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Groundwater systems adjacent to saline water bodies (whether lakes or the ocean) are usually of mixed salinities, in which fresh water flows above saline water, with a fresh–saline water transition zone in between. This mixed aquifer zone is also referred to as the *subterranean estuary* (Moore, 1999). The special conditions of various salinities in this environment result in water–rock interactions, which affect the concentrations of nutrients, trace metals, radium isotopes and other radioisotopes in coastal waters (e.g. Moore, 1996; Charette and Sholkovitz, 2002; Kelly and Moran, 2002). Charette and Sholkovitz (2006) studied the geochemical processes, affecting trace element concentrations in the subterranean estuary of Waquiot Bay, northeastern US. They described the chemical reactions that control the studied trace element distributions as redox-controlled and adsorption–desorption processes which may also be interdependent. The residence time of the groundwater in the Waquiot Bay subterranean estuary is relatively short (days to weeks, Charette and Sholkovitz, 2006), therefore it may not experience long-term water–rock interactions. The longer circulation in the Dead Sea aquifer (years to tens of years, below) allows the tracking of both short- and long-term processes.

Groundwater age is determined by various methods such as CFC's, ^{3}H, and ^{3}H/^{3}He for young groundwater (Plummer et al., 1993), while ^{14}C (Michael, 1980), and ^{4}He accumulation rate (e.g. Marine, 1979) are used for older groundwater. Seawater intrusion has also been dated using ^{14}C (e.g. Sivan et al., 2005; Yechieli et al., 2009), however dating hypersaline brines is more complex and only preliminary work has been done (Avrahamov et al., 2010).

Any radionuclide that is produced from the aquifer solids and has a known behavior during water–rock interaction may be used as a groundwater dating tool. Two important considerations are the ability to track the changes in the radionuclide concentrations along the flow path and that the radionuclide half-life fits the time scale of the groundwater flow.

The objective of this study is to determine groundwater ages and velocities, as well as the rates of water–rock interactions that occur during Dead Sea water circulation in the aquifer. In order to do so, we develop here two novel dating approaches for seawater circulating in the aquifer. While the Na/Cl ratio is unique to the Dead Sea system, the method based on ^{228}Ra may be applied elsewhere.

1.1. Radon and radium isotopes

Due to their different half-lives, radium isotopes may be used as a powerful dating tool which could be further used in the determination of the rates of geochemical processes. There are four naturally occurring radium isotopes, with half-lives ranging from 3.7 days to 1600 years. Two of them, ^{226}Ra and ^{223}Ra, are the radioactive progeny of uranium isotopes (^{238}U and ^{235}U, respectively), while ^{228}Ra and ^{224}Ra are the decay products of ^{232}Th. ^{228}Ra decays to ^{224}Ra via ^{228}Th (and the short-lived ^{228}Ac). ^{226}Ra disintegrates into ^{222}Rn, which is a noble gas. In groundwater, all four radium isotopes are produced from the aquifer solids, while in surface water they are produced by the decay

of their insoluble parents on particulate matter. In fresh water, radium is mostly tightly bound to the surface of the sediment grains (e.g. Webster et al., 1995; Gonneea et al., 2008; Lazar et al., 2008) while in saline water it is much more soluble and readily undergoes ion exchange with other adsorbed cations (e.g. Krishnaswami et al., 1991; Moore, 2000; Sturchio, 2001). The adsorption distribution coefficient (K_d) of radium in the hypersaline water of the Dead Sea was found to be very low (maximum 0.06 L/Kg), while it increases with decreased salinity (up to ~ 1 in the fresh groundwater, Kiro et al., 2012).

Several studies modeled radium and other uranium series nuclides using a one dimensional mass balance equation in order to characterize the effect of different parameters and hydrological conditions on the concentrations of the radionuclides in groundwater (Davidson and Dickson, 1986; Tricca et al., 2001). Krest and Harvey (2003) also used the same mass balances in order to quantify recharge and discharge in wetland sediments.

1.2. The Dead Sea hydrological system

The Dead Sea is a terminal hypersaline lake with salinity of 340 g/L. Its chemical composition is Ca-chloride ($[Ca/(SO_4 + HCO_3)]_{eq} > 1$) with a low Na/Cl molar ratio compared with ocean water (0.21 and 0.86, respectively). This composition is derived from ancient brines, which are the residues of seawater that intruded the rift valley and went through evaporation and halite precipitation (Smith, 1974). Other processes of water–rock interaction, such as the dolomitization of carbonates in the adjacent aquifer, further altered the original composition.

The Dead Sea is highly enriched with radium relative to most natural water bodies. The Dead Sea activities of both ^{226}Ra ($\sim$147 dpm/L, Stiller and Chung, 1984; Kiro et al., 2012) and ^{228}Ra (1–2 dpm/L, Somayajulu and Rengarajan, 1987; Kiro et al., 2012) are 2–3 orders of magnitude higher than in the ocean. Dead Sea water is also supersaturated with respect to gypsum, anhydrite, barite or celestine ($\Omega = 1.42$, 1.94, 11.75 and 2.48, respectively, Reznik et al., 2009). Nevertheless, it seems that neither barite nor celestine precipitate in the lake, not even after the Dead Sea water evaporates by a factor of 4 (Zilberman-Kron, 2008). However, during seawater circulation in the aquifer, Ba, ^{226}Ra and Sr are evidently removed from the Dead Sea water, probably mainly due to barite and celestine precipitation (Kiro et al., 2012).

The Dead Sea water level has been decreasing during the past fifty years, due to human intervention in its water budget, reaching a decline rate of more than 1 m/y. In accordance with the lake level drop, its major element composition also changed since the 1970's due to halite precipitation and mixing with end brines released from the Dead Sea potash industries. Na/Cl ratio decreased from 0.3 to 0.21, while Mg/K ratio increased from 9 to 9.8 (Gavrieli, 1997; Reznik et al., 2009).

This study focuses on the alluvial aquifer adjacent to the Dead Sea which is in direct hydraulic contact with the lake along most of its shoreline. It mainly consists of clastic fan delta deposits (gravel, sand and clay) intercalated with