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Trace elements (Li, B, Mn and Ba) as sensitive indicators for salinization and freshening events in coastal aquifers

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ABSTRACT

The current global intrusion of seawater into coastal aquifers causes salinization of groundwater and thus significant degradation of its quality. This study quantified the effect of seawater intrusion and freshening events in coastal aquifers on trace elements (Li, B, Mn and Ba) across the fresh-saline water interface (FSI) and their possible use as indicators for these events. This was done by combining field data and column experiments simulating these events. The experiments enabled quantification of the processes affecting the trace element composition and examination of whether salinization and freshening events are geochemically reversible, which has been seldom investigated.

The dominant process affecting trace element composition during salinization and freshening is ion exchange. The results of the experiments show that the concentrations of major cations and Li^+ were reversible during salinization and freshening, whereas B, Mn^{2+} and Ba^{2+} were not. During salinization, Li^+ and B were depleted due to sorption by 10 and 100 $\mu mol \cdot L^{-1}$, respectively, to about half of their expected conservative concentrations. The relative depletion of Li^+ increased with distance from the shore, representing the propagation of salinization. Ba^{2+} and Mn^{2+} were desorbed from the sediment during salinization and enriched by tenfold in the aqueous phase compared to their concentration in seawater (~0.1 $\mu eq \cdot L^{-1}$). During freshening both were depleted by almost tenfold compared to their concentration in fresh groundwater (~0.7 $\mu eq \cdot L^{-1}$). The depletion of Mn^{2+} is a sensitive marker for freshening because Mn^{2+} has a strong affinity to the solid phase. Moreover, this study shows that both Mn^{2+} and Ba^{2+} can be used as sensitive hydrogeochemical tools to distinguish between salinization and freshening events in the FSI zone in coastal aquifers.

1. Introduction

1.1. Salinization and freshening events

Seawater intrusion is defined as the migration of salt water from the sea into a fresh water aquifer (Freeze and Cherry, 1979), and is one of the main causes for the degradation of groundwater quality in coastal aquifers. The transition zone between the salt water and fresh groundwater is known as the fresh-saline water interface (FSI). Salinization due to seawater intrusion can be defined as the movement of the FSI toward the land. Freshening is the inverse event during which the aquifer is flushed by fresh water. It can be defined as the repulsion of the FSI toward the sea. Quantifying the effect of salinization and freshening on the chemical composition of the water is important for management of coastal fresh groundwater. The severe shortage in water in many coastal areas is expected to cause farther over-pumping and thus movement of the FSI inland. This is an important issue especially due to expected global climate change which can cause a decrease in recharge and a rise in sea level. This may result in elevated FSI in various locations, depending on several factors such as topography (e.g., Yechieli et al., 2010).

One of the important factors in aquifer management is the reversibility of processes occurring as a result of seawater intrusion. Whether salinization and freshening events are reversible from the hydrological point of view is debatable (e.g., Werner et al., 2013). It is clear that contamination of coastal aquifers due to seawater intrusion evolves quickly, while freshening of aquifers by flushing of fresh groundwater takes a longer period of time (e.g., Adorni-Braccesi et al., 2000; Foster and Chilton, 2003). A good example for studying seawater-intrusion reversibility is the study of seawater intrusion in Israel. Intense salinization of the central area of the coastal aquifer in Israel (Tel-Aviv) occurred between 1934 and 1948 (Zilberbrand et al., 2001). Thus, pumping was reduced in 1959 and fresh water was injected into the aquifer in 1964, but the FSI was not pushed seawards (Mandel and Goldenberg, 1986).

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However, in 1999 it was noted that the FSI retreated in some areas in the coastal aquifer of Israel (including Tel-Aviv) (Melloul and Zeitoun, 1999).

The main known geochemical effect of seawater intrusion into coastal aquifers (salinization) and flushing of the aquifer (freshening) is cation exchange, which is the sorption and desorption of cations on and from the sediment of the aquifer (e.g., Andersen et al., 2005; Appelo et al., 1990; Jones et al., 1999; Russak and Sivan, 2010; Valocchi et al., 1981). If the amount of sorption or desorption during salinization of a certain cation is equal to the amount of the inverse process during freshening, this indicated the geochemical reversibility of salinization and freshening. One of the objectives of this study is to evaluate the geochemical reversibility of salinization and freshening events.

1.2. Trace elements in the FSI

Recent studies have shown that trace elements are affected by ion exchange during salinization and freshening events. During seawater intrusion dissolved Li^+ and boron (B) are depleted due to sorption (Jones et al., 1999). On the other hand, during freshening dissolved Li^+ is enriched (Stuyfzand, 1992). Other studies showed that the dissolved B concentration increases during freshening (Ravenscroft and McArthur, 2004) and decreases during salinization (Faye et al., 2005).

Cation exchange is also suggested to be the dominant process controlling the changes of Fe^{2+}, Mn^{2+} and Ba^{2+} during seawater intrusion and freshening events in the Netherlands (Stuyfzand, 1992). Fe^{2+}, Mn^{2+} and Ba^{2+} ions were mobilized during seawater intrusion, whereas during freshening the concentrations of dissolved Mn^{2+} and Fe^{2+} declined (Stuyfzand, 1992). For Fe^{2+} and Mn^{2+} enrichment, dissolution of minerals such as siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$) was suggested as an explanation. Barite ($BaSO_4$) dissolution was excluded as a possible explanation for Ba^{2+} enrichment because the North Sea water is supersaturated with respect to barite (Stuyfzand, 1992). Changes in Fe^{2+} and Mn^{2+} at or below the FSI were also attributed to redox reactions (Charette et al., 2005; Windom et al., 2006). Fe^{2+} and Mn^{2+} were later oxidized when the saline groundwater moved upward (Charette et al., 2005). A similar phenomenon was observed in soil aquifer treatment (SAT), where under suboxic conditions manganese oxides were reduced and when groundwater reached oxic conditions, Mn^{2+} was sorbed on aquifer sediments (Oren et al., 2007). Using column experiments, it was concluded that sorption of Mn^{2+} mostly controls the fate of Mn^{2+}, although up to 20% of the removed Mn^{2+} was via precipitation as $MnCO_3$ (Goren et al., 2012).

Barium enrichment in saline water in the Hudson estuary was also explained by cation exchange (Li and Chan, 1979). Other studies found high concentrations of Ba^{2+} in saline groundwater and deduced that this occurred due to cation exchange (Charette and Sholkovitz, 2006; Shaw et al., 1998). Interestingly, authors of these studies noticed that the enrichment is most clearly observed in the mixing zone. Furthermore, in Brazil (Patos-Mirim Lagon area) the groundwater is enriched with Ba^{2+} as well, and the explanation for that was desorption and dissolution of minerals (Windom and Niencheski, 2003). Mn^{2+} oxide dissolution under anoxic condition was suggested to release Ba^{2+} to groundwater (Charette et al., 2005; Charette and Sholkovitz, 2006). It was concluded that the aquifer acts as a Ba^{2+} sink for fresh groundwater and as a source for saline waters and that saline groundwater can supply Ba^{2+} to coastal oceans (Moore, 1999).

The main objective of this research was to examine the potential use of the trace elements – Li, B, Mn and Ba – as indicators for distinguishing between salinization and freshening events. This was tested by combining field work and column experiments simulating salinization and freshening events. The controlled conditions in the experiments – salinization/freshening regime, known and constant water velocity, known natural end members' composition, known pore volume and continuous sampling - enabled quantification of the processes occurring during salinization and freshening.

2. Methods

2.1. Study site and field sampling

The study area was the coastal aquifer of Israel, which is located along the eastern Mediterranean coastline. The aquifer's geological section consists of alternating layers of calcareous sandstone (Kurkar), red loam (Hamra), and marine clays of Pleistocene age (Issar, 1968), which overlie impervious marine clays of Pliocene age (the Saqiye Group). The field work was conducted in the Nizzanim Nature Reserve (Nizzanim) that is located near Ashdod (Fig. 1). Groundwater samples were collected from a set of monitoring wells that were located perpendicular to the shore line (112b, 112S and 112 W) at different distances from the shore (40, 70 and 220 m, respectively) (Fig. 1).

The field samplings were conducted at the end of the summer, the dry season (September 2011) and in the winter, the rainy season (January 2012). Samples from borehole 112b were taken using thin tubing (3 mm I.D., 40 m) mounted on a peristaltic pump. The volume of the tube (500 mL) was pumped and removed prior to collecting a sample. The depth of the water table in 112S and 112 W was more than 10 m, thus, these boreholes were sampled by a submersible pump (Grundfos). One volume of the tube (about 5 L) was pumped and removed before sampling. Sampling began only after the electrical conductivity (EC) had reached stable values. A seawater sample from the shore area near 112b was taken in January 2012. Major ions, Br^-, Li^+ and B were analyzed from the same subsample. Subsamples for trace metals (Fe^{2+}, Mn^{2+} and Ba^{2+}) were acidified by nitric acid (0.1 N final concentrations). All samples were kept refrigerated (4 °C) until analyses.

2.2. Laboratory experiments

A column experiment (10 cm I.D., 30 cm) was conducted using aquifer sediments, fresh groundwater and seawater taken from the Nizzanim area. The sediment represents the Israeli Coastal Aquifer: calcareous sand, consisting almost 90 wt.% quartz (0.7–0.9 mm sized), 10 wt.% calcium carbonate, 0.5 wt.% clay and 0.5 wt.% organic matter. The sediment was packed slowly by depositing small amounts of the original sand sample (with no prior drying) by spoon into thin layers (~1 cm) of water.

The experiment was conducted under anaerobic conditions to simulate the natural conditions in the saline groundwater. It was maintained by purging N_2 gas, which contained an atmospheric level of CO_2 (~300 ppmv), into the water tank (fresh groundwater or seawater). The CO_2 was used in order to replace the original dissolved CO_2 that had been removed from the water due to the purging. A peristaltic pump was used to keep a flow rate of about 1 $mL \cdot min^{-1}$ from the water tank through the column. The water was flowing from the column through a small vial (~5 mL), designed for constantly monitoring the DO level by using DO electrode, and than the water flowed out through the tubes to be sampled. The experiment lasted for about a month.

The experiment simulated seawater intrusion (salinization) by replacing fresh groundwater by seawater and then flushing the seawater by fresh groundwater (freshening). The column was flushed by fresh water before the salinization part of experiment was conducted in order to ensure that the pore water in the column was saturated with the experimental fresh groundwater end-member. It should be noted that fresh groundwater for the experiment was taken in two sampling campaigns. The concentration of Mn^{2+} was different between the first and second end-members (0.5 and 0.8 $\mu eq \cdot L^{-1}$, respectively). More detailed information about the experimental design is found in Russak et al. (2015a).

2.3. Examination of the reversibility of cation exchange during salinization and freshening

In order to determine if the salinization cycle is reversible, the amount of cations sorbed and desorbed during salinization should be