

A hydrogeochemical approach for identifying saltwater intrusion processes in a leaky confined aquifer (SE Spain)

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ABSTRACT

Three boreholes were drilled and monitored, with the aim of determining the evolution of seawater geochemistry during the process of marine intrusion. The boreholes were aligned perpendicular to the Mediterranean coastline and within 30 m of it, in Almería city. Groundwater was sampled periodically from a sandy-silty layer 65 - 70 m below sea level. The samples from quaternary detrital aquifer indicated their hydrochemistry to be that of seawater with a dilution of between 15 and 40%. This result cannot be explained solely as the consequence of mixing between fresh and salt water. Rather, the water is modified through ion exchange processes with the aquifer substrate. Accordingly, ions such as K^+ and Mg^{2+} are impoverished, whilst Ca^{2+} is markedly enriched, giving percentages of between 60 and 80% of the theoretical value. The fraction of exchange (β_i) was calculated for samples ranging from seawater to fresh water, based on the major elements, and this analysis revealed that the differences in β_i could explain the hydrochemistry of the mixing zone.

INTRODUCTION

The experiments were carried out in the margin of delta of Andarax river (Almería, SE Spain). The design of the sampling array consisted of a pumping borehole and two control piezometers perpendicular to the coast line, situated so as to create a drawdown in the dynamic level of the aquifer to favour seawater intrusion. Piezometer P2 lies 4 m from the coastline, piezometer P1 lies at a distance of 24 m, and the pumping borehole (Pb) at 27 m (Fig. 1). This placement was designed to intercept the flow path from the sea to the production borehole.

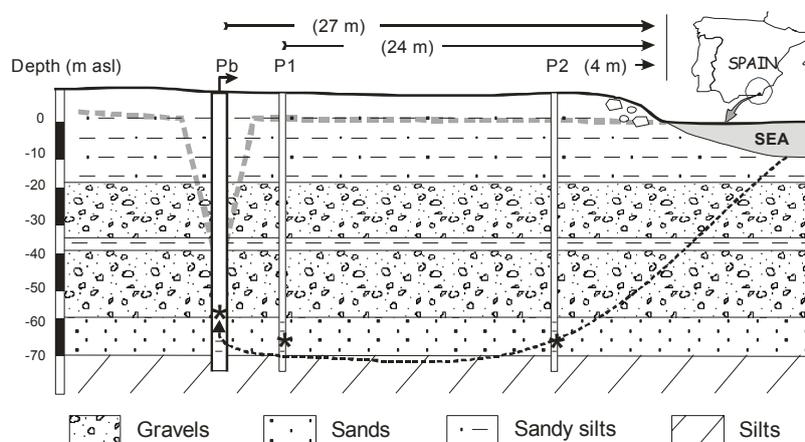


Figure 1. Scheme of the experimental control device showing the characteristics of the aquifer. The asterisk (*) marks the depth from which samples were collected (dotted line: hypothetical flow path).

The strata penetrated by the boreholes indicate an aquifer that is semi-confined by an 18-metre thick layer of sandy silts. Below there are 40 m of gravels containing marly intercalations and 10 m of sands and sandstones with intercalations of gravels and silts. The base of the aquifer is made of dark Pliocene silts at a depth of 70 m (Fig. 1).

The electrical conductivity logs from the boreholes indicate the presence of a layer of water with lower conductivity values (8 to 10 mS/cm) in the top 30 m of the aquifer. Below this zone there is a broad mixing band that extends to the base of the aquifer, with conductivities always below that of seawater. The samples were taken from a depth of 65 to 70 m below sea level. The percentage of seawater at this depth, calculated from the chloride concentration of the samples was between 60 and 85%.

METHODS

Weekly samples were taken from the three boreholes and seawater. The pump in the production borehole has been in continuous operation since early March 2009, abstracting a flow of 23 L/s. In the two piezometers, samples were taken using a small-diameter portable pump, pumping for 30 minutes before taking the sample to ensure that the sample was truly aquifer water and not standing water from the piezometer column. Samples were analysed in the laboratory accredited by the Spanish Geological and Mining Institute (IGME).

RESULTS AND DISCUSSION

The results of the analysis were used to calculate the ionic deltas of the major elements (Fig. 2). This calculation is done by comparing each constituent with its theoretical concentration for the relative percentages of fresh and seawater calculated from the chloride ion (Fidelibus *et al*, 1993; Pulido-Leboeuf, 2004; Andersen *et al*, 2005).

$$[Y]_T = [Y]_m \cdot x + [Y]_d \cdot (1-x) \quad \Delta Y = [Y]_R - [Y]_T$$

where

$[Y]_T$: theoretical concentration of an ion.

x : percentage seawater calculated.

$[Y]_m$: concentration of ion in seawater.

ΔY : delta value of an ion

$[Y]_d$: concentration of ion in fresh water.

$[Y]_R$: actual concentration of an ion.

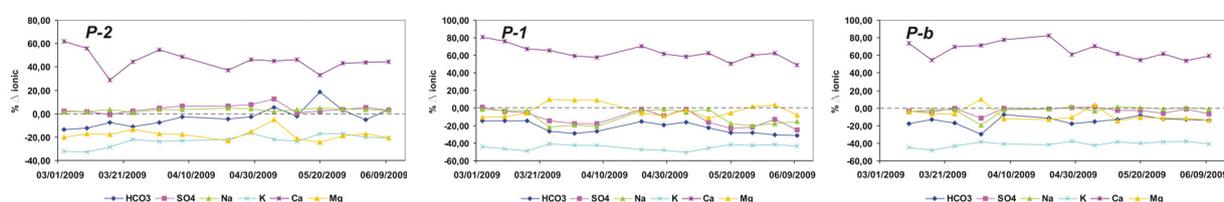


Figure 2. Evolution of the ionic deltas during the period of pumping for the three boreholes.

The results obtained vary according to the borehole in question. The general trend is of strong enrichment in calcium, which tends to diminish over the period of sampling, with values 60 to 80% above the expected concentration. Ions like Mg^{2+} and, especially, K^+ are impoverished, with percentages as low as 40% of the expected result in the case of K^+ (Fig. 2).

The main process that can explain these variations away from the expected concentrations is cation exchange between the water and the aquifer matrix. The cation exchange capacity (CEC) of the aquifer level from which the samples were taken is high, given the high percentage of clay-sized particles (approximately 10%), and an organic carbon content of around 0.2 %. According to the empirical formula of Breeuwsma *et al.* (1986):

$$CEC(\text{cmol/Kg}) = 0,7 \cdot (\% \text{ clay}) + 3,5 \cdot (\% \text{ organic carbon})$$

The value CEC is 7.7 cmol/Kg dry sediment. Knowing the density of the aquifer material (2.65 g cm^{-3}) and its porosity (30%), one can calculate the CEC that corresponds to 1 L groundwater. The CEC value thus obtained is 500 meq/L. Knowing the capacity for cation exchange of the substrate, one would have to know the cation exchange value for each of the ions and see if the CEC of the substrate is high enough to satisfy this exchange capacity. These calculations use the equivalent fraction of the exchanging major ions (β_i), plus an additional parameter ($K_{Na/i}$) to indicate the exchange coefficient for each ion with respect to Na. The major elements that take part in the exchange process are Na^+ , K^+ , Ca^{2+} and Mg^{2+} .

According to Appelo and Postma (1996): $\beta_{Na} + \beta_{Ca} + \beta_{Mg} + \beta_K = 1$

$$\beta_{Na}^2 \cdot \left(\frac{[\text{Mg}^{2+}]}{K_{Na/Mg}^2 \cdot [\text{Na}^+]^2} + \frac{[\text{Ca}^{2+}]}{K_{Na/Ca}^2 \cdot [\text{Na}^+]^2} \right) + \frac{\beta_{Na} \cdot [\text{K}^+]}{K_{Na/K} \cdot [\text{Na}^+]} + \beta_{Na} - 1 = 0$$

$$\beta_{Mg} = \frac{\beta_{Na}^2 \cdot [\text{Mg}^{2+}]}{K_{Na/Mg}^2 \cdot [\text{Na}^+]^2} ; \beta_{Ca} = \frac{\beta_{Na}^2 \cdot [\text{Ca}^{2+}]}{K_{Na/Ca}^2 \cdot [\text{Na}^+]^2} ; \beta_K = \frac{\beta_{Na} \cdot [\text{K}^+]}{K_{Na/K} \cdot [\text{Na}^+]}$$

Solving these equations give the values of β_i shown in Table 1.

Table 1. Equivalent fraction of the exchanging major ions

	Sea Water (SW)	P2	P1	PB	Fresh-Water (FW)
β_{Na}	0,589	0,557	0,457	0,506	0,103
β_{Mg}	0,263	0,241	0,296	0,269	0,376
β_{Ca}	0,082	0,157	0,215	0,198	0,514
β_K	0,066	0,046	0,030	0,035	0,033

El value of cation exchange of each of the ions, will be given by the difference of β_i between the different water types along a flow path ($\Delta\beta_i$) (Sivan *et al.*, 2005). Positive values of $\Delta\beta_i$ indicate impoverishment, whilst negative values indicate enrichment by leaching from of the aquifer matrix. In general, the cation fractionation between seawater and fresh water in the aquifer gives values of $\Delta\beta_i$, coinciding with the trend observed for the ionic deltas calculated for the chloride ion. A trend of impoverishment in Na and K ions is observed and an enrichment in Mg and Ca (Table 2).

Table 2. Values of ion exchange at different sites in the aquifer and the potential exchange for cations (meq/L) between seawater and freshwater.

	SW - FW	SW - P2	P2 - P1	P1 - PB	PB - FW	(SW-FW)* CEC (meq/L)
$\Delta\beta_{Na}$	0,487	0,032	0,100	-0,049	0,403	243
$\Delta\beta_{Mg}$	-0,113	0,022	-0,055	0,027	-0,107	57
$\Delta\beta_{Ca}$	-0,432	-0,075	-0,058	0,017	-0,316	216
$\Delta\beta_K$	0,033	0,020	0,016	-0,005	0,002	17

This trend is not observed in piezometer P1, and this could be because there is poor connection with the aquifer at this point, as indicated by an uranine tracer test undertaken in the study area. Multiplying these values of $\Delta\beta_i$ by the CEC calculated (500 meq/L) we obtain the potential

for cation exchange (in meq/L) for each chemical element. The values obtained exceed the ionic delta value calculated for the chloride ion, and so these deltas can be explained by the cation exchange.

The evolution observed in the capacity for cation exchange of each ion, from seawater to fresh water, can be deduced from the values of $\Delta\beta_i$ obtained in the various analyzed samples (Fig. 3). For Na, it is observed that during the intrusion process, there is adsorption by the substrate; this is more and more pronounced as the flow line moves inland. In contrast, fixing of the potassium ion is especially marked over the first few metres of the intrusion, becoming negligible close to the pumping borehole. In the case of the Mg ion, at first adsorption is observed, but from piezometer P2 inland, desorption occurs. For calcium, there is a gradually increasing trend for the aquifer matrix to liberate this element. These trends in the evolution of the $\Delta\beta_i$ may explain the differences between the ionic deltas observed in each of the boreholes.

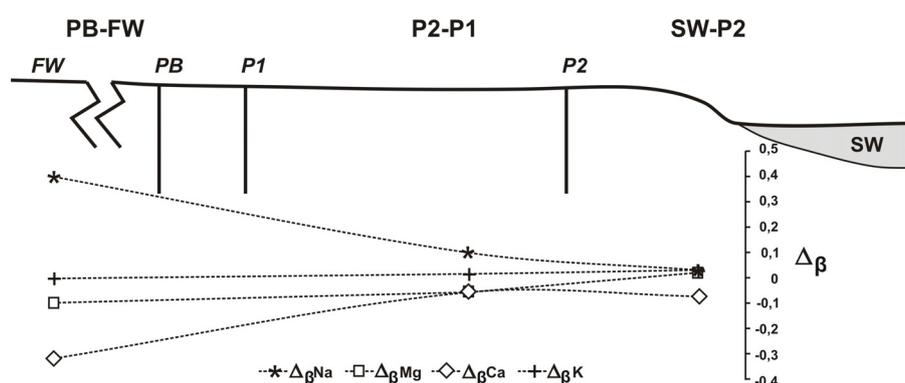


Figure 3. Evolution of the $\Delta\beta$ of the major ions over the intrusion flowpath.

Acknowledgements: This work was undertaken within the framework of project 017/SGTB/2007/2.1. funded by the Spanish Ministry of the Environment and project CGL2007-63450/HID by the Spanish Ministry of Science.

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