

Brackish springs in coastal aquifers and the role of calcite dissolution by mixing waters

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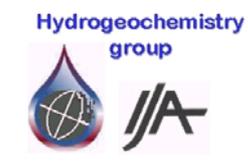
**APPENDIX A: Tracing salinity sources of
S'Almadrava karstic brackish spring (Mallorca,
Spain) with sulfur and oxygen isotopes**

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**PhD Thesis
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ABSTRACT:

S'Almadrava spring (Mallorca Island) is a good example of a brackish spring in a highly karstified coastal carbonate formation. It is located at 6 m.a.s.l. and discharges water of variable salinity, depending on the discharge regime. Its average flow rate is 12.3 hm³/y, and the electric conductivity can reach 40 mS/cm. The phenomenon has been explained as the result of seawater intrusion into the karst system, but discussions still remain on whether this is the unique source of salinity. The objective of this study is to elucidate the role of other possible salinity sources, such as dissolution of Keuper evaporites or fertilizers. The methodology is based on the analysis of concentration, and $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of dissolved sulfate in a series of samples collected during a high-frequency sampling campaign. Analyses of isotope data show an excellent agreement with a conceptual model of pure mixing of seawater intruding a freshwater aquifer. The influence of other potential sources of salinity, if any, has been estimated to be very limited at any stage of the spring hydrological cycle.

1 INTRODUCTION

Brackish karstic springs are a frequent phenomenon in Mediterranean coastal carbonate formations. They have the common feature of discharging water of variable salinity above sea level. S'Almadrava spring is located in the north-eastern coast of Mallorca Island, and is an outstanding example of these springs. It discharges about 2 km inland and at an elevation of 6 m.a.s.l. (Fig. 1). The aquifer feeding the spring is formed by highly karstified Liasic calcareous materials. Both karst and storm-like recharge appear to control the groundwater regime.

The spring shows high annual discharges of 12.3 hm³/y in average, and a very irregular regime, from sharp peaks after rain events to drying up after a rainless period (normally in summer). Salinity is also variable, with values ranging from 4 to 40 mS/cm of electric conductivity (EC). As in other reported springs, EC tends to increase when flow rate decreases, but what makes S'Almadrava unique is that the highest values of EC are associated with the beginning of the sharp discharge events after a long dry period. This high and variable salinity prevents human use of this important reserve of water in an area with a large water demand, especially in summer.

The potential use of the discharged water has promoted several studies of the spring, but

unfortunately only a few have been published. The phenomenon has been explained as the result of seawater contamination into the karst system (Baron & Gonzalez 1978; Cardoso 1997).

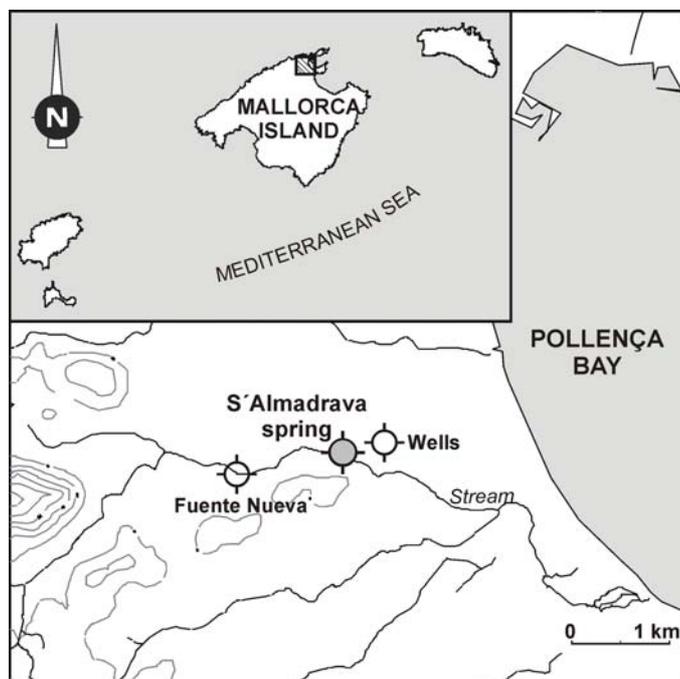


Figure 1. Geographic situation of S'Almadrava spring and location of samples presented in this study.

Thus, mixed freshwater-seawater would discharge above sea level because the excess elevation (6 m) is balanced by the excess in density

of seawater above that of the mixture. This explains why salinity increases with decreasing discharge. Also, during a long dry period, freshwater head drops, allowing seawater to flow further into the aquifer, thus leading to higher salinity waters on the next discharge (Sanz et al. 2003). Moreover, as shown in Fig. 2, a secondary salinity peak is developed in the middle of the sharp salinity drop after every new rainfall event, which illustrates the hydraulic and geochemical complexity of the karst system feeding the spring. .

Although it is clear that seawater must contribute to the spring salinity, discussions still remain as to whether this is the unique source of salinity. Thus, Cardoso (1997) suggested that dissolution of Keuper evaporitic materials appearing at the base of the carbonated main aquifer may contribute to salinity, especially when the spring dries up and the residence time in the aquifer increases. Anthropogenic sources of salinity like fertilizers may also contribute somehow. However, discussions have always been based on a limited number of electrical conductivity and dissolved chloride measurements, and major ionic relations. These techniques could not discriminate minor sources of salinity in the spring, if any, and this issue has remained unconfirmed over the years.

The objective of this study is to elucidate the sources of water salinisation based on the analysis of concentration, and $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of dissolved sulfate. As the isotopic composition of sulfur and oxygen is nearly constant in present-day seawater, and dilution processes do not affect the sulfur isotope ratio, these analysis provide an excellent tool for quantifying the potential salinity sources.

2 MATERIALS AND METHODS

A series of samples were collected during a campaign in November 2004 with a frequency of two samples a day. This campaign covered the first spring discharge after a long, dry summer period, and a complete cycle of the spring behavior until a new rainfall event occurred. Figure 2 shows the hydrological and salinity trends during the high frequency sampling campaign. Eight samples from this campaign representing the main features of the spring discharge were selected for this study (Fig. 2). This series of samples was augmented with three additional samples from S'Almadrava spring collected in a previous campaign, three samples from salinized wells in a radius of 200 m around the spring mouth, and one more sample collected in a non-salinized spring (Fuente Nueva) located about 1 km farther inland along the same groundwater flow path. Local seawater at Pollensa bay was also sampled.

Electrical conductivity and pH were measured in situ during sampling. Samples were immediately filtered with a Millipore filter of 0.45 μm pore size and stored in a cold environment. Sulfate concentration was analyzed by HP liquid chromatography. For sulfur and oxygen isotope analysis the dissolved sulfate was precipitated as BaSO_4 by the addition of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in acid media ($\text{pH} < 2$) to prevent BaCO_3 formation (Soler et al. 2002). The sulfur isotopic composition was determined from BaSO_4 with an elemental analyzer (Carlo Erba 1108) coupled in continuous flow with a isotope ratio mass spectrometer -EA-IRMS- (Finningan MAT Delta C). The oxygen isotopic composition was measured in duplicate by on-line pyrolysis with a ThermoQuest TC/EA unit coupled with a isotope ratio mass spectrometer -TC-EA-IRMS- (Finningan MAT Delta C). Notation is expressed in terms of δ per mil (‰) referred to V-SMOW (Vienna Standard Mean Oceanic Water) for oxygen and V-CDT (Vienna Canyon Diablo Troilite) for sulfur. The isotope ratios were calculated using international and internal laboratory standards. After correction of the mass spectrometer daily drift, with standards systematically interspersed in analytical batches, precision was 0.2‰, for sulfur and 0.5‰ for oxygen.

3 RESULTS AND DISCUSSION

The results of the analysis are summarized in Table 1. The potential sources of dissolved sulfate in the S'Almadrava spring considered in this study are seawater, Keuper evaporites (Upper Triassic) at the base of the carbonated aquifer, and anthropogenic fertilizers used in the recharge area. The sulfate composition of rainwater in the spring's recharge

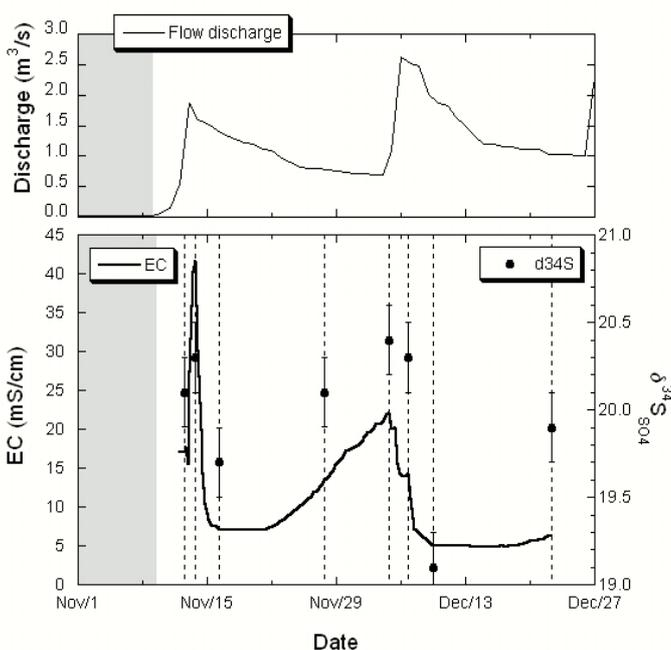


Figure 2. Discharge and EC of S'Almadrava discharge during the sampling period. Shaded area shows the period with no flow discharge. $\delta^{34}\text{S}$ analysis are represented at their sampling time (marked with dashed lines).

area is below 10 ppm in average, although values up to 37 ppm have been measured (Cardoso 1997), and therefore this component has not been considered in this study.

Local seawater sulfate has a sulfur and oxygen isotopic composition of 21.7 and 9.5 ‰, respectively (LSW on Table 1), slightly higher –but consistent– than other values reported in the literature (20.0 and 8.6 ‰ (Claypool et al. 1980) and 21.0 and 9.5 ‰ (Clark & Fritz 1997) for standard seawater; 20.6 and 9.5‰ for western Mediterranean Sea (Soler et al. 2005) (WMD on Table 1));. In the following discussion, the seawater sulfate composition was considered to be an average of the local and western Mediterranean values (aveSW on Table 1). According to Utrilla et al. (1992), the average sulfur and oxygen isotopic composition of the Keuper evaporites of the Iberian peninsula is 13.4 ± 1.48 and 11.8 ± 1.72 ‰, respectively. The range isotopic composition of anthropogenic fertilizers was defined on 5.0 ± 4.7 ‰ for sulfur and 12.0 ± 2.8 ‰ for oxygen by Vitòria et al. (2004). Sulfur isotope content becomes higher with EC in the spring cycle (Fig. 2) while Oxygen isotope content shows the opposite behavior (not shown). Small variations in δ may be attributed to the fact that total sulfate concentrations are likewise variable.

Table 1: Analysis results for the samples used in this study.

Location	Label	Date	SO4 mg/L	$\delta^{34}\text{S}_{\text{SO4}}$ ‰	$\delta^{18}\text{O}_{\text{SO4}}$ ‰
S'Almadrava spring	JAB-3	11/9/2001	522.61	20.09	9.13
S'Almadrava spring	JAB-6	11/21/2001	20.00	10.05	9.22
S'Almadrava spring	SAL1	12/6/2002	1105.33	21.30	nd
S'Almadrava spring	M03-2	11/12/2004	816.78	20.06	9.78
S'Almadrava spring	M03-8	11/13/2004	1946.29	20.35	9.83
S'Almadrava spring	M03-17	11/16/2004	260.19	19.68	10.02
S'Almadrava spring	M03-50	11/27/2004	676.22	20.11	9.79
S'Almadrava spring	M03-74	12/4/2004	794.34	20.43	9.80
S'Almadrava spring	M03-81	12/6/2004	517.40	20.31	10.09
S'Almadrava spring	M03-84	12/9/2004	123.32	19.13	10.12
S'Almadrava spring	M03-110	12/22/2004	211.69	19.86	9.80
Well AlmaSup.10m	ASUP-10	12/6/2002	551.28	20.30	nd
Well AlmaSup.87m	ASUP-87	12/6/2002	895.91	21.40	nd
Well AlmaInf.13m	AINF-13	12/6/2002	587.17	20.60	nd
Fuente Nueva spring	JAB-112	11/30/2002	32.45	6.34	7.27
Pollença Bay	LSW	12/6/2002	2754.50	21.70	9.50
West Mediterranean	WMD		2700*	20.60	9.50
Average Seawater	aveSW		2727.25	21.15±0.55	9.50
Iberian Keuper	Keuper		1004**	13.44±1.48	11.76±1.72
Fertilizers	Fertilizers			5.0±4.7	12.0±2.8

nd = not determined, *: (Hem 1985); **: water equilibrated with gypsum at 25°C. Data sources: WMD (Soler et al. 2005); Keuper (Utrilla et al. 1992, N=21); and Fertilizers (Vitòria et al. 2004, N=22).

Figure 3 shows the mixing models of the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ content of average seawater, Keuper evaporites and Fuente Nueva spring, which is considered to represent the freshwater end-member feeding the spring. Mixing percentages for each model on Figure 4 are normalized to sulfate concentration of the sample. It is shown that all the samples from S'Almadrava spring appear very close to the

seawater end-member and do not align clearly with any of the mixing lines drawn. This situation does not improve if we consider the uncertainty range of the mixture end-members and the samples themselves. One of the S'Almadrava spring samples aligns clearly in the mixing line of Fuente Nueva and Keuper materials but with an estimated mixing ratio below 5% and therefore this sample can be considered essentially freshwater. Moreover, this sample contains 59 ppm of nitrates suggesting a possible minor influence of fertilizers as well.

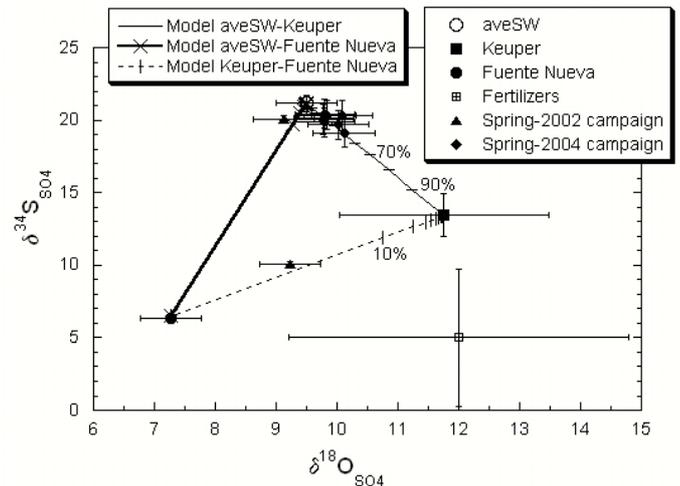


Figure 3. Mixing models of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ content in average seawater and either Iberian Keuper or anthropogenic fertilizers.

The variation in $\delta^{34}\text{S}$ versus sulfate concentration of the analysed samples is presented in Figure 4. Samples with the highest sulfate concentration have the highest $\delta^{34}\text{S}$ but isotope compositions show a very small variation for a broad range of sulfate concentration (Fig. 4). This distribution is compatible with a mixing process between two end-members with different isotope composition and sulfate concentration.

Accordingly, a mixing curve has been calculated following the expression of Faure (1986) for two-component mixtures (Fig. 4). As for one the mixing models on Figure 3, freshwater from Fuente Nueva and average seawater (JAB-112 and aveSW, on Table 1) were selected as end-members in the mixture. Figure 4a shows that all S'Almadrava spring samples from the two sampling campaigns match the mixing line calculated for sulfur content, thus identifying the end-members controlling the composition in the spring. Samples from salinized wells also show a very good agreement with the fresh-seawater mixing model presented (Fig. 4a). It is important to note that, regardless the uncertainty in its sulfate concentration, the isotopic signature of the Keuper evaporites (also represented in Fig. 4) does not show any relationship with the mixing process. The oxygen isotopic composition shows a behavior similar to that of sulfur with a good matching of the freshwater-seawater mixing model proposed (Fig. 4b).

to be very limited at any stage of the spring behavior, including long-dry periods.

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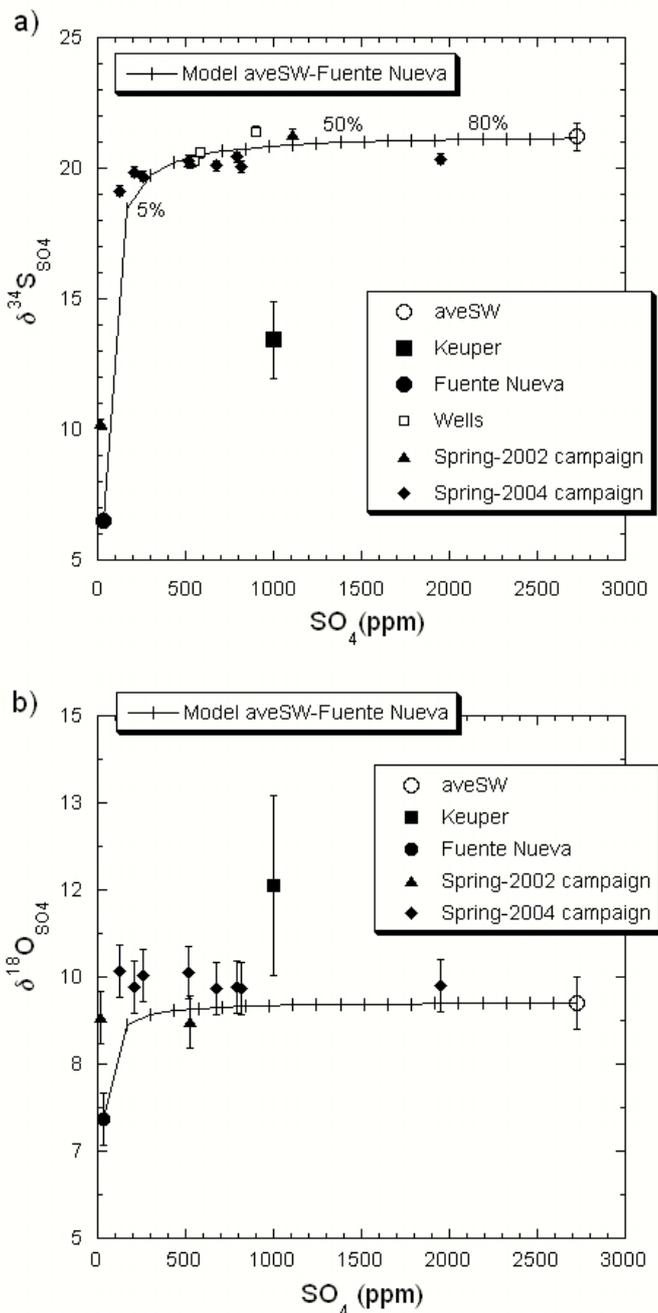


Figure 4: a) Mixing model for $\delta^{34}\text{S}$ versus sulfate concentration; b). Mixing model for $\delta^{18}\text{O}$ versus sulfate concentration. The end members are freshwater from Fuente Nueva spring and average seawater (samples JAB-112 and aveSW, respectively, on Table 1).

4 CONCLUSIONS

According to isotope data the main source of dissolved sulfate in S'Almadrava brackish spring is seawater. Analyses of waters from the spring show an excellent agreement with a conceptual model of pure mixing of seawater intruding the aquifer with the freshwater of the aquifer. The influence of other potential sources of salinity like Keuper materials or anthropogenic fertilizers, if any, has been estimated