IAH selected paper

Evaluating mineral water quality trends of Pedras Salgadas (Portugal)

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Abstract

The mineral waters of Pedras Salgadas are located in the North of Portugal in fractured rock formations associated with different types of granites. Their genesis is related to the great fault system of Penacova-Régua-Verin. These waters are hypo-thermal, naturally carbonated with values of free CO_2 between 500 mg/l and 5800 mg/l. TDS ranged from 384 mg/l to 5415 mg/l and the hydrochemical facies is bicarbonated-sodium. In order to detect the trends and the rate of change of some main physical-chemical parameters a seasonal Mann-Kendall test was applied to a sequence of monthly values, observed in 5 wells, from 1995 to 2005. To estimate the rates of change per unit time, a robust estimator of the trend slope was also calculated by Thiel and Sen regression method.

INTRODUCTION

Portugal is one of the richest E.U. countries in what concerns mineral waters. The carbonated waters are a very particular group of natural mineral waters, being Vidago-Pedras Salgadas hydro-mineral field one of the most important Portuguese concessions. This group contributed with 31956000 euros to the Portuguese economy, which reveals the importance of these waters in the group of the carbonated waters bottled in Portugal.
In spite of some specific studies, there is still a growing need to apply adequate tools that permit a proper quantitative/qualitative evaluation of these waters, being one of the main objectives to analyse correctly the temporal evolution of the main physicochemical parameters in terms of the magnitude of their trends.

STRUCTURAL GEOLOGY OF VIDAGO/PEDRAS SALGADAS REGION

The existing carbonated waters in mainland Portugal are located in the northern area of the Hesperic Massif, namely in the middle Galiza-Subzone (see fig.1). Their geographical location is well correlated with regional fault systems such as the “Penacova-Régua-Verin Fault”, “Vilariça Fault” and “Rio Minho Fault”. They emerge on the granites and schist, usually on the intersection between the great regional faults and their conjugates, because it is normally on these sites that the best conditions for the rising of the fluids from the deep zones of the crust exist.
The presented carbonated waters are related with the great fault Penacova-Régua-Verin (with a NNE-SSW direction), which is long and deep and affects the entire continental crust. The carbonated springs occur mainly in the W branch of the fault, and sometimes in their conjugate WNW-ESSE, emerging on areas where the post-tectonic granitoid rocks are dominant.
The structural features which greatly influence the hydro-mineral trajectories are largely discussed in Ribeiro (1992); however, and according to Carvalho (1993), the recharge areas and the conditions of in-depth circulation are not completely understood. The tectonic model of Ribeiro (1992) points out the recharge areas in Padrela mountain and in E border of the tectonic depression. Notwithstanding, the isotopic study made by Palma (1993) suggests “the recharge area of the mineral aquifer is situated south of the emergencies themselves and might be connected with the surface of Alvão or the surface of Padrela”. Same suggestion was made by Costa (1992) that considers that the mineral water acquires the principal’s characteristics through a deep circulation in tectonic accidents SSW-NNE / S-N, being

the differences of chemical patterns resultant of a set of reactions that, in the slow ascension of the water during the phase of discharge of the hydro-mineral aquifer, develop with different intensities; according to this author the alterations that has been observed, most of all derived from the exploitation regime of exploration of the carbonated waters, point in this direction.

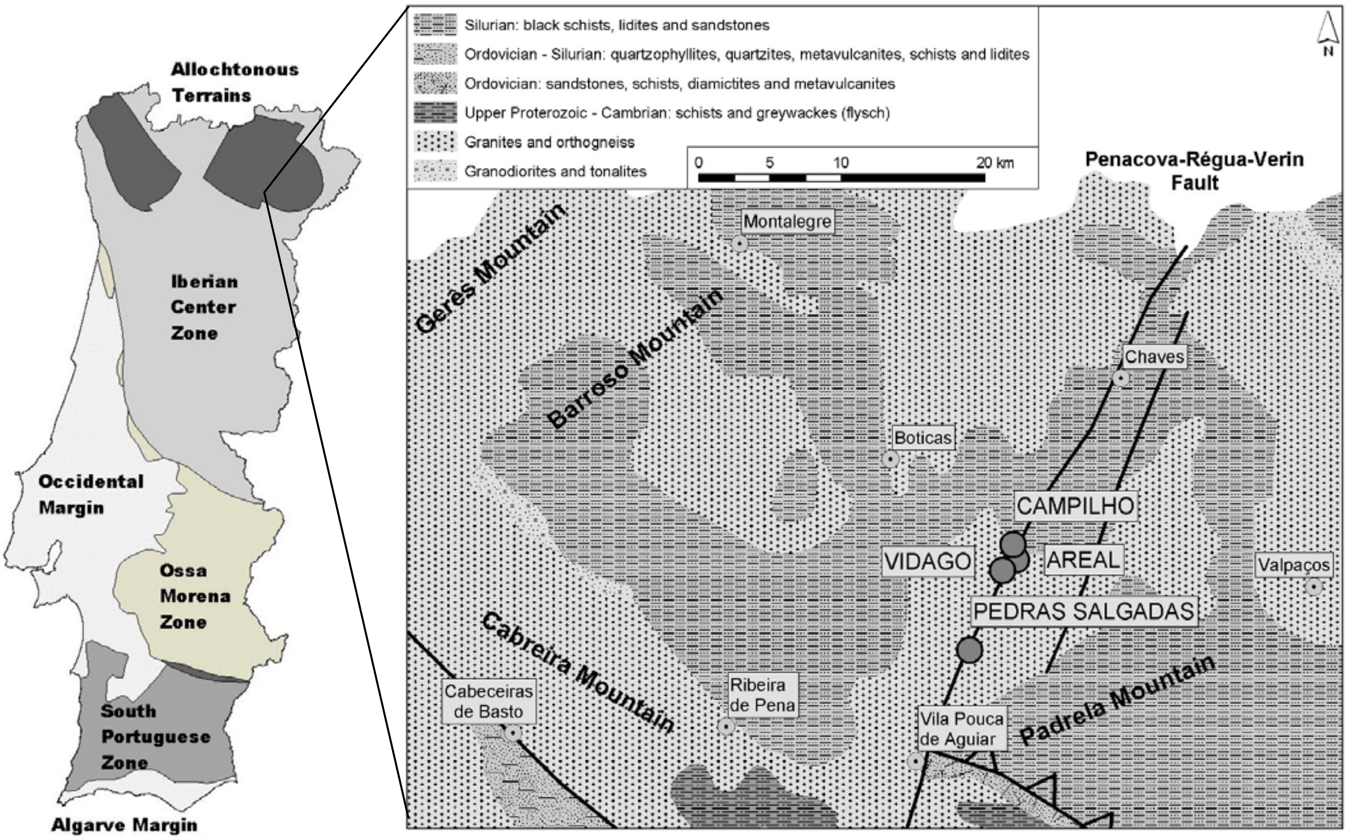

Figure 1 –Location of Vidago-Pedras Salgadas hydro-mineral field in Portugal. (source:INETI)

WELL MONITORING

In Pedras Salgadas concession exist 4 carbonated water wells and 3 natural springs legalised as natural mineral water. Notwithstanding, the extraction of mineral water is only made through 4 wells (AC 12A, AC 13, AC 17 and AC 25) with a depth that varies between 70 m (well AC12) and 185 m (well AC25). Well AC12A was build in 1998, replacing AC12, whose water revealed some physical-chemical instability, aspect that was already verified in Ribeiro and Lourenço (1999). The natural springs mentioned above are part of a study of regular monitoring made by the concessionaire with the objective to evaluate the available mineral resource.

A monitoring program was carried out by the ex-Portuguese Geological-Mining Institute, since 1986 consisting on 3 to 4 simple physical-chemical analyses per year and one complete analysis every 4 or 5 years. For this trend analysis, observations ranging from 1995 to 2005 were used. Each observation consists on information of the following variables: F^-, CO_2, SiO_2, Cl^-, HCO_3^-, SO_4^{2-}, Na^+, Mg^{2+} and Ca^{2+}.

EXPLORATORY AND VISUALIZATION DATA ANALYSIS

Mineral waters of Pedras Salgadas are hypo-thermal, naturally carbonated, with values below 20ºC (at surface) and with a rich content in Na^+ (fig. 2). Analysing figures 3 to 6, we concluded that median contents of HCO_3^- are from 403 mg/l to 3175 mg/l, with a maximum value of 4087 mg/l detected in AC25 (fig. 3) and median concentrations of Na^+ between 148 mg/l (AC13) and 931.50 mg/l (AC25).

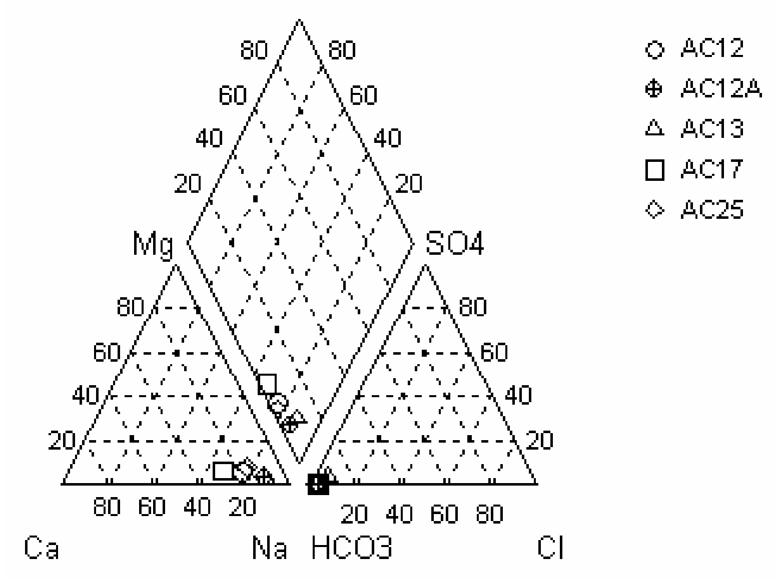

Figure 2 – Piper diagram of carbonated waters of Pedras Salgadas

The highest F^- concentrations were found in well AC13 (median equal to 4.5 mg/l). On the contrary the lowest values of CO_2 were observed in the same well (median equal to 712.5 mg/l) opposing to AC 25 where a median of 4955 mg/l was determined.
In short, we can say that well AC25 depicts water with the most mineralized properties, in opposition to the hydrochemical facies observed in AC13. The physical-chemical parameters, which values present the highest dispersion are CO_2 and HCO_3^-, followed by Na. AC25 is also the well that presents the largest variation of these parameters.

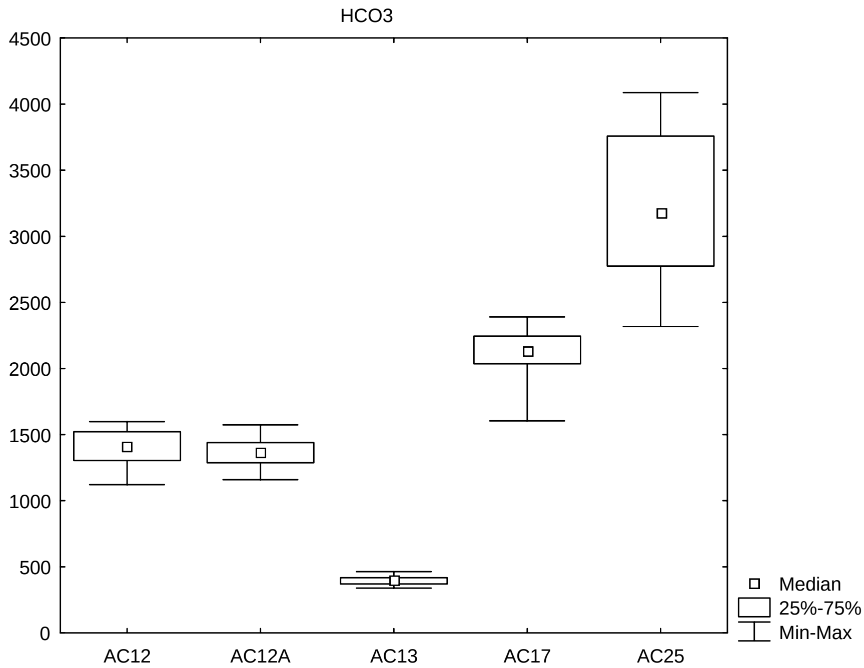

Figure 3 – Multiple box-plots of HCO_3^- (mg/l) calculated for the 5 wells

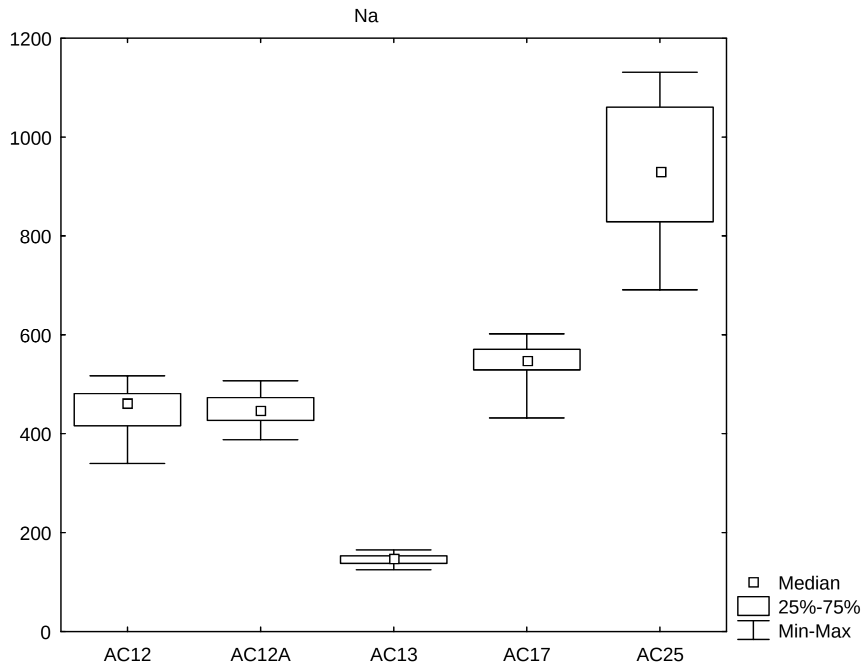

Figure 4 – Multiple box-plots of Na^+ (mg/l) calculated for the 5 wells

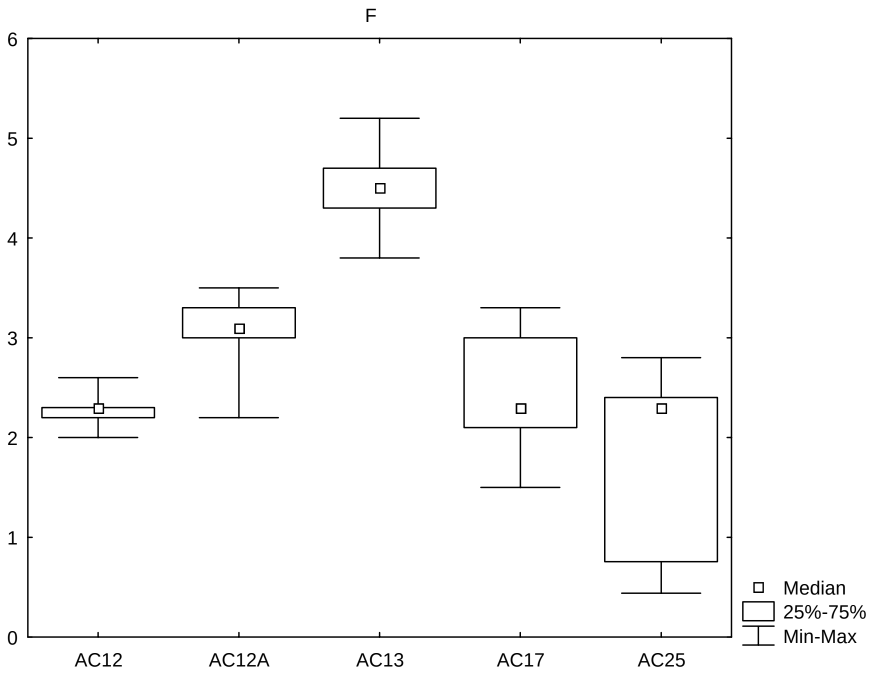

Figure 5 – Multiple box-plots of F^- (mg/l) calculated for the 5 wells

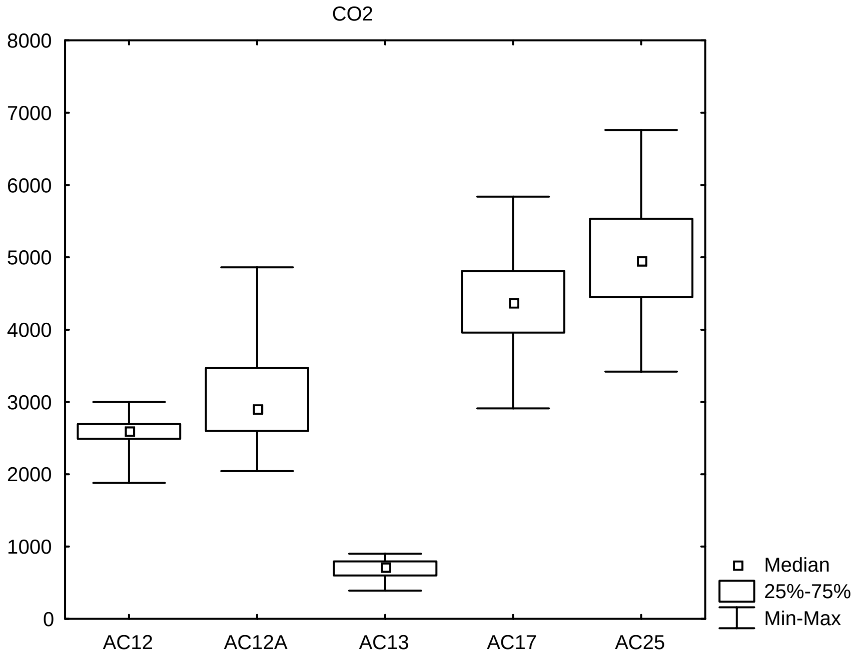

Figure 6 – Multiple box-plots of CO_2 (mg/l) calculated for the 5 wells (mg/l)

For a first visualisation of the temporal evolution of each parameter the correspondent time series were plotted for each parameter. For instance figure 7 shows in general a downward trend of the parameter HCO_3^- in the 5 cases, with special evidence in AC17 and AC25 wells.

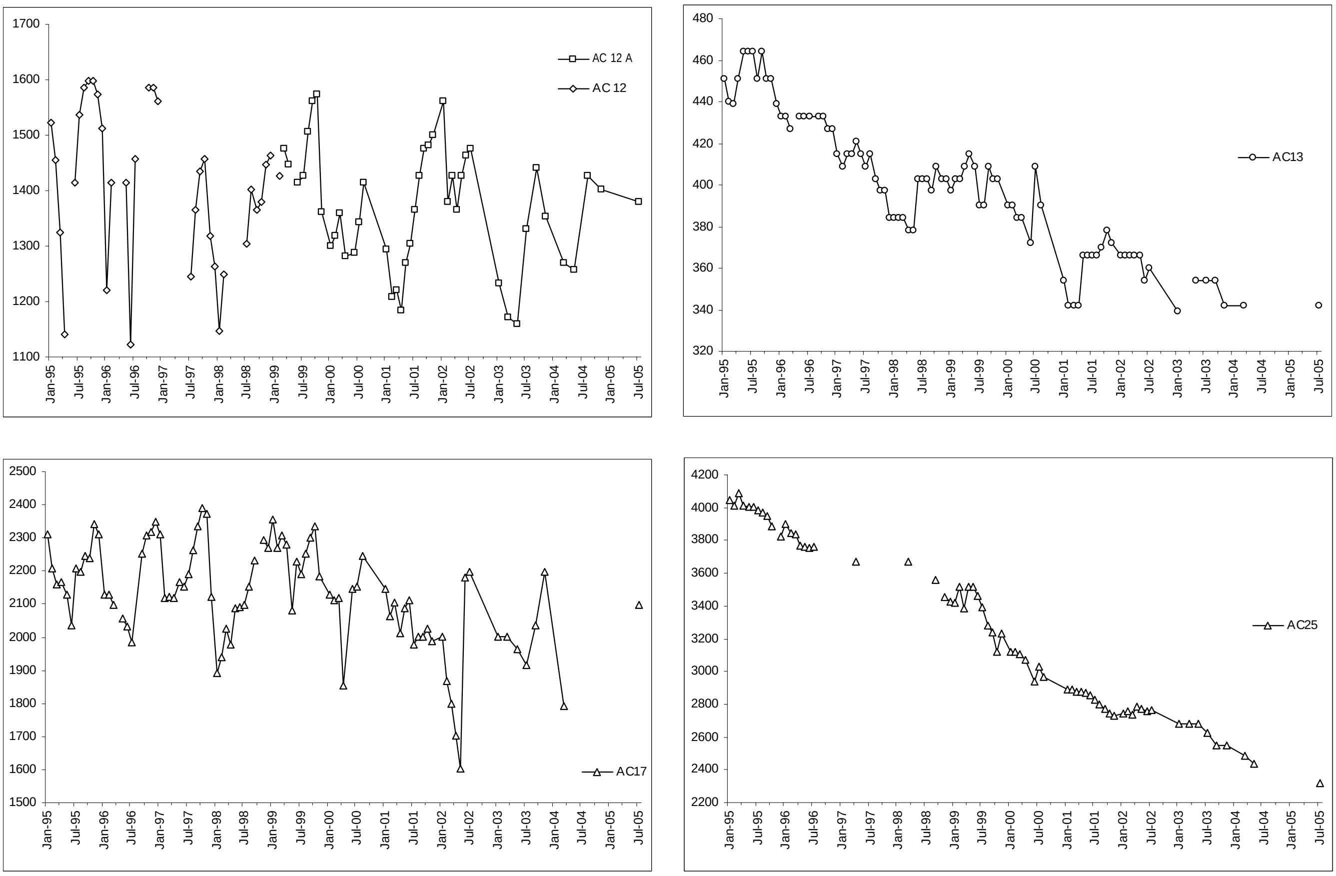

Figure 7- Temporal evolution of HCO_3^- (mg/l) in AC12, AC12A, AC13, AC17 and AC25 wells

TREND ANALYSIS

Methodology

The Mann-Kendall test is a non-parametric statistical method mainly used to detect and assess the trends of the water quality parameters (Hirsch *et al*., 1982). The selection of a non-parametric approach is particularly suitable to analyse data exhibiting one or more of the following properties: free distribution, missing values, presence of outliers, seasonality or censored data.
The test is applied to a sequence of observation ordered by time $q_1, q_2, \ldots, q_n$, where a parameter S is build according to the following expression:

$$S = \sum_{k<j} f\ (q_j - q_k) \tag{1}$$

Where:

f is a function defined by: $f(\theta) = 1$ (if $\theta > 0$); $f(\theta) = 0$ (if $\theta = 0$) and $f(\theta) = -1$ (if $\theta < 0$)

A null hypothesis H_0 of no trend is tested and rejected or confirmed according to the statistical distribution. To measure the strength of the upward or the downward trend a statistic p is calculated. In general trends are considered statistically significant when $p<0.1$. For this study a seasonal Mann-Kendall test procedure will be used and an estimation of the correspondent slope will be performed by a robust regression suggested by Thiel and Sen.

Using this technique, the slope of the trend is given by the median (B) calculated on the basis of all the values d_{jk} following:

$$d_{jk} = (q_j - q_k) / (j - k) \quad (2)$$

for all the pairs q_K with $1 \leq k < j \leq n$

The trend slope is expressed by change per unit time and is related with S by:

If $S>0$ then $B \geq 0$;

If $S < 0$ otherwise.

The test can be applied with other techniques in a joint methodology in order to achieve a particular objective (Ribeiro and Macedo, 1995).

Results and discussion

The non-parametric test was applied to the mineral waters of Pedras Salgadas, to the period from January 1995 to July 2005 in a monthly basis. Observations of the physical-chemical parameters listed above were used for this purpose.

Table 1 displays the results of the detected upward, downward or no trends, the estimated slope (change per month) and the statistical p.

From the analysis of this table the following features may be highlighted:

a) In the majority of the wells, significant downward trends ($p < 0.1$) were detected in the following water quality descriptors: Cl^-, Na^+, Mg^{2+}, HCO_3^- and Ca^{2+}.
b) In some wells, however, significant upward trends were also observed in F^- (wells AC13, AC17 and AC25) and SO_4^{2-} (AC12, AC13 and AC25).

In what concerns the magnitude of the estimated slopes we should emphasize the decrease of 14.93 mg/l per month of HCO_3^- calculated in AC25. However such high value should be interpreted according to the relative high median values obtained in this well when compared with the other cases.

Table 1 – Water quality trends in Pedras Salgadas

Wells Parameters	**F^-**	**CO2**	**SiO_2**	**Cl^-**	**HCO_3^-**	**SO_4^{2-}**	**Na^+**	**Mg^{2+}**	**Ca^{2+}**
AC 12 (till 1998)	0.00 ↔ 0.46	-4.86 ↓ 0.21	-0.12 ↓ 0.01	-0.10 ↓ 0.00	-5.96 ↓ 0.00	0.01 ↑ 0.07	-1.37 ↓ 0.21	-0.05 ↔ 0.12	-0.41 ↓ 0.00
AC12A (from 1998)	0.00 ↔ 0.86	7.71 ↔ 0.20	0.05 ↑ 0.06	-0.02 ↓ 0.04	-1.42 ↔ 0.15	-0.02 ↓ 0.04	-0.41 ↓ 0.02	-0.02 ↓ 0.03	-0.08 ↓ 0.17
AC13	0.004 ↑ 0.00	-3.02 ↓ 0.00	-0.03 ↓ 0.00	-0.01 ↓ 0.01	-1.00 ↓ 0.00	0.08 ↑ 0.00	-0.28 ↓ 0.00	-0.02 ↓ 0.00	-0.05 ↓ 0.00
AC17	0.01 ↑ 0.00	-7.57 ↓ 0.00	-0.02 ↔ 0.17	-0.04 ↓ 0.00	-1.63 ↓ 0.00	0.00 ↔ 0.42	-0.30 ↓ 0.00	-0.05 ↓ 0.00	-0.29 ↓ 0.00
AC25	0.02 ↑ 0.00	3.52 ↔ 0.29	-0.04 ↓ 0.00	-0.15 ↓ 0.00	-14.93 ↓ 0.00	0.04 ↑ 0.00	-3.62 ↓ 0.00	-0.30 ↓ 0.00	-1.02 ↓ 0.00

legend:

0.01: slope (per month)
↑ upward trend ↓ downward trend ↔ no trend
Statistic p = 0.00

A stability of the temporal evolution of these parameters should be expected in this hydro-mineral field and not the occurrence of significant upward and downward trends detected in all parameters and in the majority of the wells. This situation maybe caused by some exogenous influences such as the alteration of the well pumping rates. The consequences are visible in the behaviour of CO_2 and in the major and trace composition, especially HCO_3^-.

CONCLUSIONS

The temporal evolution of 9 water quality parameters monitored in 5 wells of Pedras Salgadas carbonate waters, showed significant upward and downward trends, although we considered that the estimated slopes are, in general, not important taking into account the high mineralization of these waters. The high variability in these trends detected in some parameters is closely related to the pumping system, with indirect influences in the fluctuations of the CO_2.

Lourenço (2000) revealed that, on the contrary of the wells, the natural springs of Pedras Salgadas hydro-mineral field do not show significant upward and downward trends. This fact may indicate that some of the variations verified in the wells are a consequence of the system pump, that cause variations in CO_2, and that consequently may imply a set of reactions that in turn can influences modifications in the majority and residuals component of these waters, mainly in HCO_3^-.

This is a dual phase hidrogeological system, gas and water, and the pumping process favours the separation of the two phases. Generally the system has to reach a new equilibrium, and such fact can delay some time.

Further studies should be carried out in the future in order to proper understand the influence of the alteration of pumping rates in the water quality trends detected in one of the most important hydro-mineral fields of Portugal.

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