Trend analysis using nonparametric statistical techniques for detection and evaluation of spatial and temporal chemical changes at a hydrothermal exploitation (Felgueira Spa - Central Portugal)

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Abstract Like many thermomineral springs all over Europe, Felgueira Spa (Central Portugal) sulfide alkaline water has been used in therapeutic bathing for centuries. Two periods may now be depicted in the exploitation history of those low enthalpy resources: one characterized by the use of flowing water from springs and a dug well that lasted until the 1990´s when deep drilling wells were promoted to satisfy the increasing demand of medicinal water. After that, a second period of a more active resource extraction begins. Detection of statistical significant monotonic time trends in chemical composition for the period 1991-1998 was done using nonparametric statistical techniques, namely, Spearman rank correlation coefficient and Sen´s slope estimator.
Keywords trend analysis; thermal water; chemical evolution

INTRODUCTION AND GENERAL BACKGROUND

Located at Central Portugal, Felgueira´s low enthalpy hydrothermal system corresponds to a deep circulation of meteoric water in fractured granite. Springs are located along a ENE-WSW trending fault system with water temperatures between 32 and 18 ^oC. In the early 1990's, three drilled wells (AC1, AC2 and AC3) intersecting the hydrothermal structure reaching depths of 60 – 300 m, were productive and yielded thermal hybrid waters, with temperatures from 27 to 36 ^oC.

The chemical characteristics of these thermal waters can be summarized as low content of dissolved salts (< 350 mg/L), high values of pH (around 8,20), negative redox potential (<-250 mV); Na^+ is the dominant cation and absence of any predominant anion: HCO_3^- (150 mg/L) and Cl^- (50 mg/L). Nitrate is usually below a detection limit of 0,07 mg/L, and nitrogen is present under the species $NH4^+$(0,10 mg/L). Also, presence of F^-, Li^+, low Mg^{2+} contents and sulphur in solution in the forms of SO_4^{2+} and HS^-.

Comparison of the constituents from hot springs and water wells indicates no major differences in chemical composition. This shows that all waters emerge from the same aquifer system and follow identical flow path, submitted to similar physical and chemical processes during its ascent to surface.

This paper presents a study based on sampling results and trend analysis to detect any chemical evolution of the exploited thermal water during the first years of wells production. The interest in detecting chemical trends in groundwater quality is a critical issue in assessing environmental conditions of hydrothermal systems exploitation at a sustainable basis. Considerable amounts of data from monitoring programs will begin to be available to perform such analysis.

DATA AND METHODS

Water quality data presented here come from database of the enterprise, which detains the exploitation concession of the hydrothermal system, and has a monitoring analytical program for these waters. Sampling frequency has varied over time, first on a monthly basis for the first one and half years of monitoring program and after that analyses were done three or four times per year in a more or less regular schedule. Available data covers a period from 1991 to 1998 (for AC1 and AC2 wells) and 1991 to 1996 for AC2 well.

For detection of monotonic trends in time series data a nonparametric rank based statistical test named Spearman´s ranks correlation coefficient can be used (Helsel & Hirsch, 2002). Spearman's correlation coefficient R_{sp} is calculated as:

$$R_{sp} = 1 - \frac{6\sum_{i=1}^{n} d_i^2}{n^3 - n} \tag{1}$$

where d_i is the difference in rank of a pair of variables (*x* and *y*), each containing *n* observations. In time series interpretation the independent variable stands for time.

The null hypothesis H_0: $R_{sp} = 0$ (there is no trend), against the alternate hypothesis H_1: R_{sp} < or > 0 (there is a negative or a positive trend), at a chosen level of significance α, is checked with the test statistic t_t computed by equation (2), and then compared to a table of *t* distribution with *n*-2 degrees of freedom:

$$t_t = \frac{R_{sp}\sqrt{n-2}}{\sqrt{(1-R_{sp}^2)}} \tag{2}$$

Although explicating the statistical significance of the correlation between variables, the above procedure does not provide an estimate of the trend magnitude. This can be approached using a nonparametric slope estimator very robust to outliers and extreme values in the time series like Sen`s slope estimator (Sen, 1968). If a monotonic trend has been detected for a variable over *n* time periods, if *y* stands for the variable tested for trend and *t* stands for the time periods, all the possible slopes for data pairs are defined as:

$$Q = \frac{y_i^{'} - y_i}{t_i^{'} - t_i} \tag{3}$$

Sen’s estimator of slope is the median of all the slopes calculated using the above equation (3). A more detailed description can be found in Gibbons (1995).

DISCUSSION

Hydrochemical data covering ten water quality parameters of sampled water from wells AC1, AC2 and AC3 may give some insights on the chemical evolution of these fluids during a period of more intensive exploitation.

Distribution comparisons between all wells for selected elements concentrations are depicted by the boxplots on Fig. 1. These plots show for AC2 and AC3 wells a stronger departure from a normal distribution for water quality parameters, specially observed in skewness but also by the presence of extreme values. AC3 medians are almost systematically different from the median of the other two wells. Therefore, there are different amplitudes of variations in water chemistry from the wells indicative of some spatial chemical changes. Water from AC1 well discloses a composition with less variance and consequently less dispersion of data. This can be interpreted as being the less hybrid water captured from the hydrothermal system.

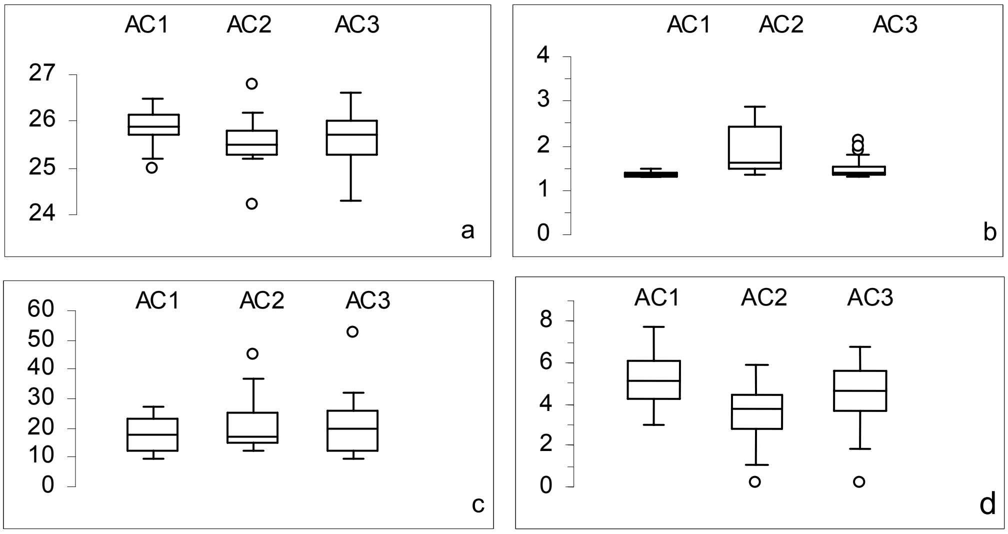

Fig. 1 Boxplots for AC1 water parameters: a) Alkalinity (mL/L HCl 0,1N); b) Hardness (p.p.10^5 $CaCO_3$); c) Sulfate (mg/L); d) Sulfide (mL/L I_2 0,01N).

Fig. 2 displays the time series of measured values of sulphate, chloride, alkalinity, sulfide and hardness at AC1 water well. With the exception of SO_4^{2-} the time series plots are inconclusive in indicating any change over time, i.e., if any trend is developing. In order to detected other possible trends a more detailed statistical analysis is required. The characteristics of data requires a nonparametric statistics as they are irregularly spaced and contain extreme values. The nonparametric technique also has the advantage of being unaffected by the distribution of the population.

Table 1 presents the results of the application of Spearman´s rank correlation coefficient (equation 1). Through this application and the Spearman statistical criterion (equation 2) we detect several monotonous increase and decrease trends in water quality parameters with time.

For AC1 and AC3 wells there is a tendency for increased parameters related to the interaction with a superficial aqueous environment (e.g. hardness, sulfate and nitrate) and a decreasing tendency for pH and constituents associated to a deep thermal environment (sulfide, alkalinity, and F^-). The conservative ions Cl^- and Li^+ remain unaffected. A relatively different pattern is noted for AC2 water well witch is also a sign of the spatial variability of the sampled waters, as already shown by boxplots of water quality parameters.

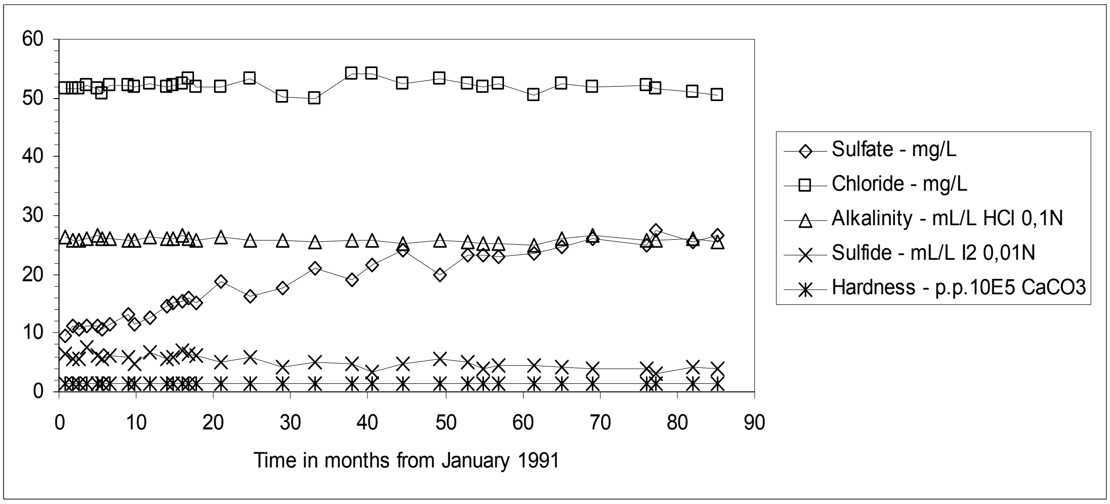

Fig. 2 Time series of water quality parameters of AC1 well.

Table 1 Results of Spearman´s test. The values in bold means that there is a trend considered statistically significant at the 5% level.

	pH	Alkalinity	Sulfide	Hardness	F^-	Cl^-	SO_4^{2-}	NO_3^-	Na^+	Li^+
AC1	**-0,758**	**-0,431**	**-0,789**	**0,808**	**-0,351**	0,050	**0,981**	**0,663**	0,357	-0,151
AC2	**-0,502**	-0,243	-0,317	**0,617**	-0,133	0,130	**0,79**	**0,397**	**0,445**	0,307
AC3	**-0,828**	**-0,627**	**-0,722**	**0,783**	**-0,617**	-0,195	**0,888**	**0,740**	**0,460**	-0,089

The highest slope value for positive trends of water constituents at AC1 was computed for sulfate that presents an increasing rate of 2,10 mg/L year^{-1}. Hardness and nitrate have a slope estimate of 0,02 of their respective measure units per year. Among the decreasing trends Sen´s estimator gives a significant value for sulfide concentration of -0,34 (mL/L I_2 0,01N per year).

CONCLUSIONS

Active exploitation of the hydrothermal system by pumped water has imposed a new dynamic equilibrium in water pressures within the productive geological structure. This amplifies the vulnerability of thermal fluids as they rise to the surface. The observed evolution can be attributable to the impact of acid mine drainage in the area. Although not problematic for the water quality parameters analysed this hybridization will stop when anthropogenic impacts disappears.

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