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Measurement and Analysis of Physicochemical Parameters Concerning Thermopylae Natural Hot Spring Waters

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Abstract: The present study describes a measuring station, implemented at the hot water source place, for collecting data of various physico-chemical factors. The integrated systems is able to continuously measure, process and transmit via a radio transmitter data regarding OPR, conductivity, water temperature and pH. An additional unit receives and stores data in convenient form for data analysis. The second part of the study presents a statistical study of the data with a time series analysis. The most important results are (1) Statistically significant correlations were found between the involved physico-chemical factors and (2) Data exhibit various periodicities.

Key words: Ground-water hydrology, hydrogeology engineering geology, modeling/statistics

INTRODUCTION

Thermopylae is a famous mountain pass in central Greece, expanding from Locris into Thessaly, located right between Mount Oeta and the sea (Maliac Gulf). It is a mandatory passage in the main north-south road of Greece known from antiquity for its natural hot water springs (the ancient Greek word Thermopylae, roughly translated, means "hot gateway"). A source of considerable economic and scientific geological interest, these underground hot water reservoirs, in the region of Thermopylae, can provide significant amounts of energy in profitable manner, via the development of suitable geothermal devices. Possible applications include the use of hot water for the heating of local buildings, spa, agricultural or industrial heating, etc.

The aim of the present study is first to describe the developed measurement system which was built in order to investigate the physical and chemical characteristics of the Thermopylae natural hot water springs. This integrated system answers to a challenge stated in (Popit *et al*., 2005), where the demand for a system of continuous monitoring of physicochemical parameters in spring waters is stated. The second target is to provide a thorough time series analysis of collected data.

Some of the early developments and preliminary findings of the presented integrated measurement station can be found in (Avlakiotis *et al*., 2007; Latsos *et al*., 2007; Verros *et al*., 2007, 2009). Zmazek *et al*. (2002) the deployment of a similar sensor network for environmental monitoring (Slovenian hot springs) as well as seismic detection is described.

A Wireless Sensor Network (WSN) consists of spatially distributed autonomous devices which cooperatively monitor physical or environmental conditions, such as temperature, sound, vibration, pressure, motion or pollutants, at different locations. A wireless sensor network is typically characterised by small-scale sensor nodes, harsh environmental conditions, mobility of nodes, dynamic network topology, communication failures, heterogeneity of nodes, large scale of deployment and unattended operation. Wireless sensor networks (Callaway, 2003; Stojmenovic, 2005; Cordeiro and Agrawal, 2006; Ilyas and Mahgoub, 2006; Iyengar and Brooks, 2004) can be employed for weather/environment parameters monitoring (Cordeiro and Agrawal, 2006; Iyengar and Brooks, 2004), seismic detection, acoustic detection, inventory tracking, health monitoring, military surveillance or process monitoring.

It is common knowledge that geological deformations which take place in different depths can create modifications in the natural setting of a specific areas and may induce modifications in the flow, thermal and chemical characteristics of thermal spring waters, such as variations in the water flow, changes in the temperature and/or chemical composition and variations both in the

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gas discharge flow-rates and in the chemical and isotopic composition of the gases (especially 222Rn), level in deep wells, hydrostatic pressure, electrical conductivity.

The observed geophysical phenomena include variations in water level in deep wells, hydrostatic pressure, water flow rate from wells, electrical conductivity and water temperature. The most frequently studied geochemical phenomena have been concentrations of dissolved gas and ions in groundwater and variations in concentrations of crustal and mantle volatiles in ground gases (Wakita, 1978; King, 1980; Nakamura and Wakita, 1985; Wakita *et al*., 1986; King *et al*., 1994; Thomas, 1988; Koch and Heinicke, 1994; Dongarra *et al*., 1995; Heinicke *et al*., 1995, 2000; Igarashi *et al*., 1995; Irwin and Barnes, 1980; Koch *et al*., 2003). In the system under study four parameters were introduced and measured which are important to geological deformations too. Measuring water temperature to study the flow rate and depth variations, pH to study the acidity variations, redox potential to study the biologic load variations and electrical conductivity to study the salanity variations.

MATERIALS AND METHODS

Developed integrated system for measurements: Precise elements of constitution of water of natural hot spring waters are important tools that are used by various researchers for the determination and the interpretation of phenomena that develop in the underground layers of lithosphere. Thermopylae is a region in central Greece noted for its rich history. In this study, the following 4 parameters of Thermopylae hot spring waters have been measured: Temperature, conductivity, pH and redox potential (ORP).

The measurement of the aforementioned parameters is performed with sensors which have been placed inside a small brook that emanates from the main hot spring. A station for the collection, processing and transmission of data has been built. This station (Fig. 1) constitutes of the following parts:

- The main unit, which consists of: A controller for collection and data processing, terminals for the measurement units, a radio-modem, a non-stop power supply system, a power sub-unit of voltage 220 V and a unit with leak-tightness specifications JR 65
- A sub-unit above a hot spring's brook, which consists of the following sensors: Water temperature measuring sensor, pH measuring sensor, conductivity measuring sensor and redox potential (ORP) measuring sensor
- A directional YAGI antenna of 8 elements

The data collection measuring station, which was described above, transmits the digital data through a wireless radio network (using the radio modem). The receiver main unit for data processing has been placed in the campus of Technological Educational Institute (TEI) of Cenral Greece, Lamia, Greece. A functional and a schematic representation of Thermopylae data collection station can be seen in Fig. 1 and 2, respectively.

In order to find the best location for placing Thermopylae measuring station for optimal operation, we have also considered the following tasks: Data sampling frequency distance between the two stations (transmitting and receiving), access in energy networks, access in telecommunications networks, easy access to the station and security.

The instruments for the online measurements include: A) A continuous flow pH-meter (B and C ELECTRONICS /PH/ORP 7685) with proportional output of p_ and temperature, B) a continuous flow instrument for the measurement of oxidative redox potential (ORP) (B and C ELECTRONICS) with proportional output of ORP and C) a data logger, a UPS for continuous power supply, a modem and a complete

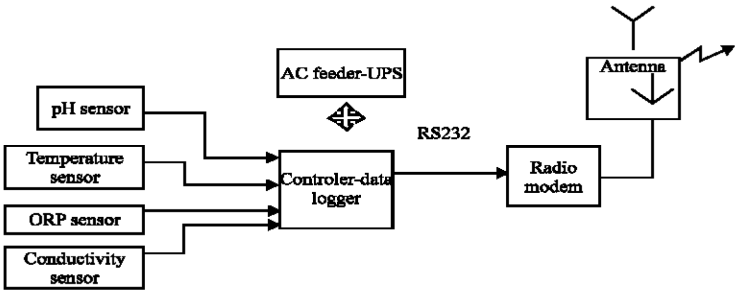

Fig. 1: Functional description of the measurement unit at the hot water source

Fig. 2: Experimental set up for the on-line measurement of pH, redox potential and temperature. Both sensors and data logger unit are shown

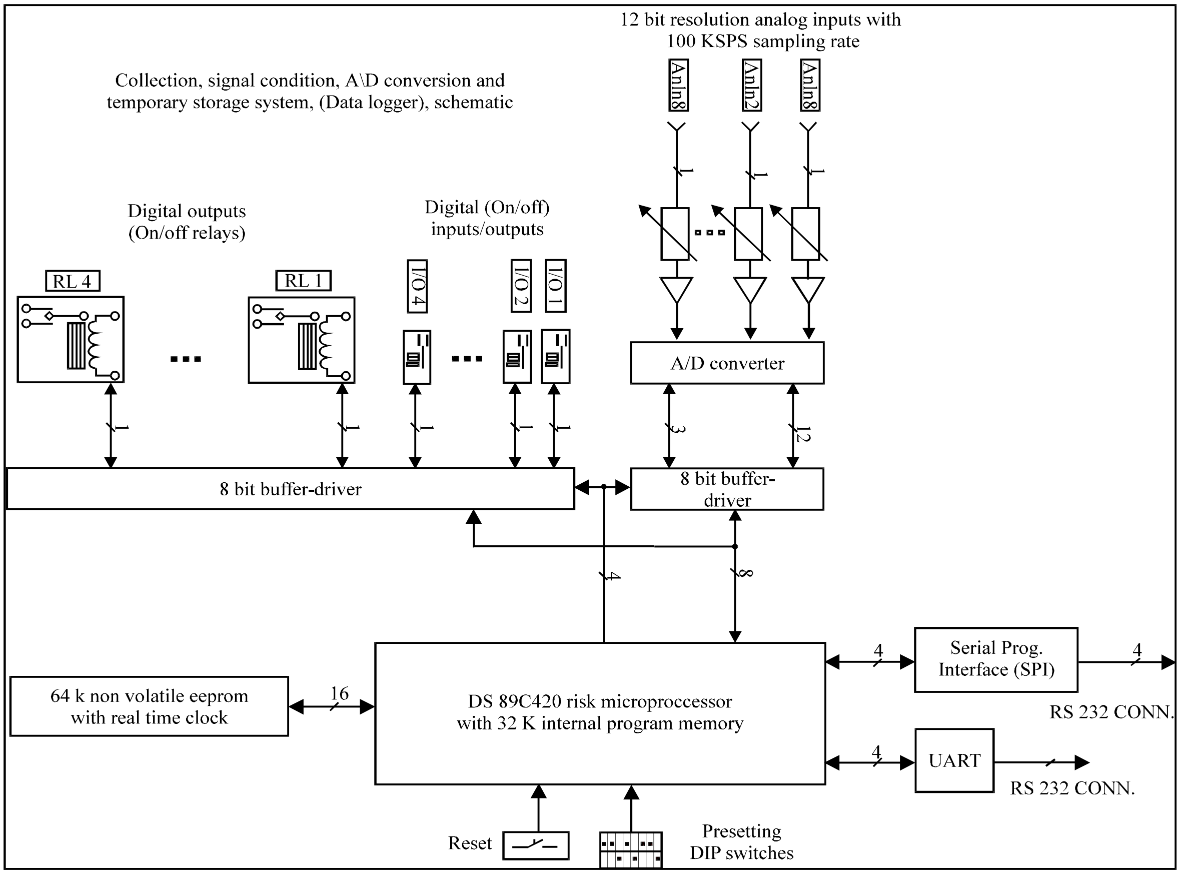

Fig. 3: Data logger functional analysis

system for the transmission of results to the Technological Institute of Lamia, few kilometers away.

Data processing: The values of the 4 measured parameters are collected using the sensors of the system and they correspond to analogue signals. The next stage is an analogue signal pre-processing (signal conditioning), while a current loop (0 to 20 mA) is used to transfer the data to the analogue inputs of a data logger unit. In this unit data is digitised with 12 bit analysis (resolution). Consequently, the digitised data is grouped in data frames, which consist of frame serial number, date and hour. Data frames are then transferred via serial port (RS 232) to the radio modem and they are transmitted using the YAGI antenna to the receiver, which is located at the university campus.

It is well known that geological phenomena vary with time. It is logical to assume that the measured physicochemical parameters also follow the same variation in time. This assumption however, does not exclude the probability that certain abrupt geological realignments might occur in a few minutes. In this case time scale of a few minutes would provide critical information for the geological phenomenon. Since, however, physicochemical parameters in this research project have been measured underwater, their values are considered to vary on a time scale of hours. However, a sampling period (or data collection time) of 15 min is considered to be adequate for the investigation of geological phenomena.

Data logger unit: A functional analysis of the data logger unit (or data collection system) can be seen in Fig. 3. Thus, it consists of the following parts:

- A unit with 8 analogue inputs (channels). Each input has the following characteristics: Variation range 4-20 mA, 12 bit resolution, highest sampling frequency 10000 samples/sec and input voltage protection 2000 V
- Four input/output lines with optocoupling and with the following characteristics: “ON” input indication corresponds to voltage range 8-10 V, while “OFF” input indication corresponds to voltage range 0-2 V. On the other hand “ON” output indication corresponds to 12 V/100 mA, while “OFF” output indication corresponds to 0 V

Central processing unit (series 8051), memory NVRAM 64 K, internal memory FLASH 16 K, two serial communication ports and power supply 220 V AC/12V DC 3 A.

Statistical methods: The measurement station in Thermopylae hot springs commenced full operation at 1/6/2010 (date) 13:00 (time). The measured parameters of hot waters are: Temperature in Celsius degrees, potential of redox (ORP) in milli-Volts, pH and conductivity in milli-Siemens. Data analysis was studied performing a set of time series methods (Makridakis *et al.*, 1983; Gardner, 1985; Bloomfield, 1976; Fuller, 1976). The SPSS v16 software was used.

A time series is a set of observations obtained by measuring variables regularly over a period of time. One of the most important reasons for doing time series analysis is to try to forecast future values of the series. A model of the series that explained the past values may also predict whether and how much the next few values will increase or decrease.

The seasonal decomposition procedure decomposes a series into a seasonal component, a combined trend and cycle component and an "error" component. The procedure is an implementation of the Census method I, otherwise known as the ratio-to-moving-average method. It is an appropriate method if a scientist is interested in analyzing periodic measurements. The goal is to determine if there is any trend in the data. In order to uncover any real trend, the scientist first needs to account for the variation in readings due to seasonal effects. The seasonal decomposition procedure can be used to remove any systematic seasonal variations. The trend analysis is then performed on a seasonally adjusted series.

In the presented study the seasonal component that was used is the additive method. The seasonal adjustments are added to the seasonally adjusted series to obtain the observed values. This adjustment attempts to remove the seasonal effect from a series in order to look at other characteristics of interest that may be "masked" by the seasonal component. In effect, trends estimates seasonal components that do not depend on the overall level of the series. Observations without seasonal variation have a seasonal component of 0.

The autocorrelation function (Bartlett, 1946; Box and Jenkins, 1976; Cryer, 1986; Quenouville, 1949) in use always shows a significant peak at a lag of 1 with a long exponential tail, a typical pattern for time series. If there is a significant peak at a lag characterized by a number N this suggests the presence of an N times the lag period seasonal component in the data. The partial autocorrelation function was also examined in order to allow a more definitive conclusion (Bartlett, 1946; Box and Jenkins, 1976; Cryer, 1986; Quenouville, 1949).

The sample autocorrelation function in use is (Eq. 1):

$$\text{acr}_k = \left[\sum_{i=1}^{n} (x_i - \overline{x})^2\right]^{-1} \sum_{j=1}^{n-k} (x_j - \overline{x})(x_{j+k} - \overline{x}) \tag{1}$$

and the sample partial autocorrelation function in use is defined from (Eq. 2-3):

$$\hat{y}_{11} = \text{acr}_1,\ \hat{y}_{22} = (\text{acr}_2 - \text{acr}_1{}^2)(1 - \text{acr}_1{}^2)^{-1} \tag{2}$$

$$\hat{y}_{kj} = \hat{y}_{k-1,j} - \hat{y}_{k-1,k-j}\hat{y}_{k,k} \quad k = 2,\dots, \quad j = 1, 2, \dots, k-1 \tag{3}$$

Where:

$$\hat{y}_{kk} = \left(\text{acr}_k - \sum_{j=1}^{k-1} \hat{y}_{k-1,j}\, \text{acr}_{k-j}\right)\left(1 - \sum_{j=1}^{k-1} \hat{y}_{k-1,j}\, \text{acr}_j\right)^{-1} \quad k = 3, \dots, \tag{4}$$

where, x_i is i-th observation of data time series, i = 1,...,n, and acr_k is the kth lag sample autocorrelation and $\hat{y}_{kk}$ is kth lag sample partial autocorrelation in Eq. 4.

Furthermore, the spectral plots procedure was used to identify periodic behavior in time series. Instead of analyzing the variation from one time point to the next, it analyzes the variation of the series as a whole into periodic components of different frequencies. In the presented analysis both smooth and unsmoothed series were estimated. Smooth series have stronger periodic components at low frequencies; random variation ("white noise") spreads the component strength over all frequencies. Unsmoothed plot of spectral amplitude (plotted on a logarithmic scale) against either frequency or period is called periodogram. Low-frequency variation characterizes a smooth series. Variation spread evenly across all frequencies indicates "white noise."

The plot of the periodogram (fast Fourier analysis) shows a sequence of peaks that stand out from the background noise.

Apart from the main peak the remaining peaks are best analyzed with the spectral density function. The produced diagram is simply a smoothed version of the periodogram, named spectral density. It is a periodogram that has been smoothed to remove irregular variation. The type of smoothing used was Tukey-Hamming. Smoothing provides a means of eliminating the background noise from a periodogram, allowing the underlying structure to be more clearly isolated. Periodic components that have the shape of a sine or cosine function (sinusoidal) show up in the periodogram as single peaks. Periodic components that are not sinusoidal show up as a series of equally spaced peaks of different heights, with the lowest frequency peak in the series occurring at the frequency of the periodic component.

In summary, we have estimated various spectral plots for each factor in order to confirm the existence of a periodic component of a time series and we have verified what significant periodicities are present. The spectral density was seen to be more useful than the periodogram for uncovering the underlying structure, because the spectral density smoothes out the fluctuations that are caused by the non-periodic component of the data.

RESULTS AND DISCUSSION

Descriptive statistical results are shown in Table 1. It can be easily observed that data concerning temperature and pH are normal distributed, while conductivity and ORP are not. However, ORP distribution can be handled as a skewed normal distribution. The various distributions of the measured quantities are shown in Fig. 4-7.

An interesting finding of our statistical analysis is the statistically significant correlations estimated among the four factors: Temperature, ORP, pH and Conductivity. However, there are only mild associations between the following factors: Temperature vs. ORP and pH vs. ORP and Temperature vs. pH. Both parametric and non parametric methods for the investigation of possible associations agree with the later as can be seen in Table 2-3.

In order to investigate further correlations we explored if there is a control variable that will reduce the correlations appeared in our analysis, Table 3. Thus, a partial correlation analysis was performed taking into account all the possible combinations of the four factors under investigation. Table 4 presents results with temperature as a control variable. This sounds possible

Table 1: Descriptive statistics

	Statistic					Skewness		Kurtosis	
Variables	Minimum	Maximum	Mean	Standard deviation	Variance	Statistic	Standard error	Statistic	Standard error
Temperature	33.6400	45.7400	40.914098	0.3178323	0.101	-0.415	0.010	7.651	0.021
ORP	-486.5000	163.6000	-388.306530	70.6846158	4996.315	3.214	0.010	15.171	0.021
pH	5.0800	8.3100	6.675395	0.1510279	0.023	0.443	0.010	21.320	0.021
Conductivity	1.8700	20.4400	11.594353	4.4818946	20.087	-0.058	0.010	-1.086	0.021

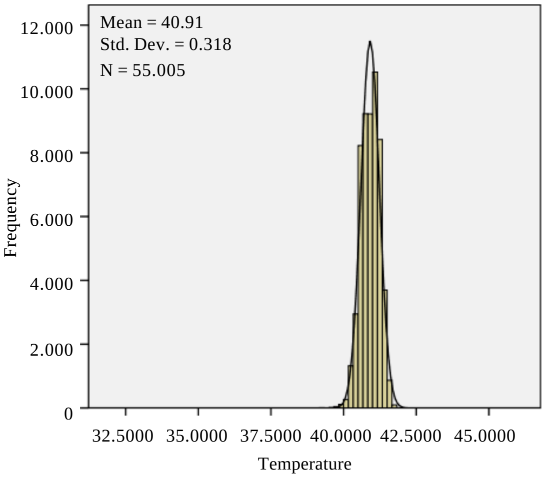

Fig. 4: Temperature distribution

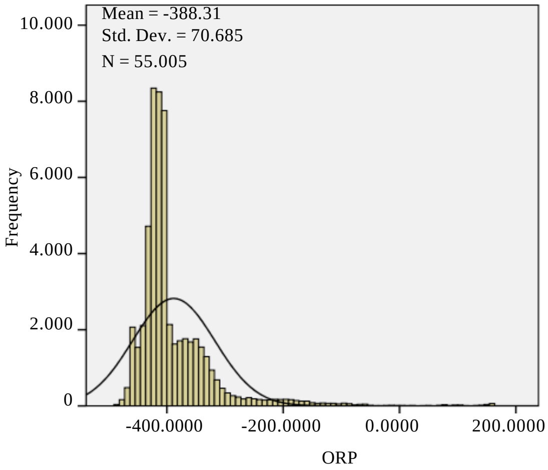

Fig. 5: ORP distribution

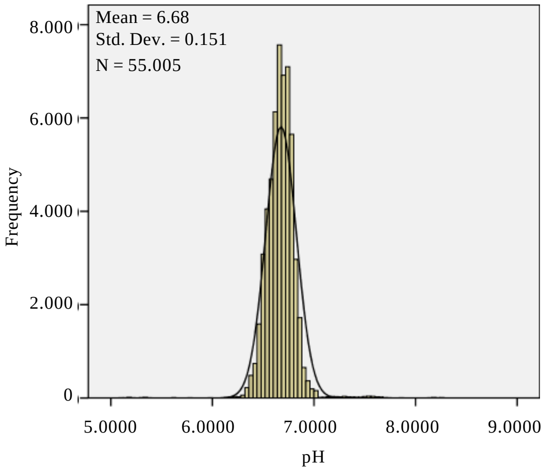

Fig. 6: pH distribution

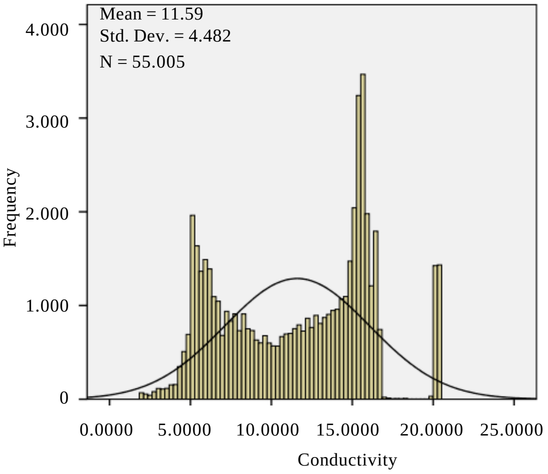

Fig. 7: Conductivity distribution

Table 2: Pearson correlations

Pearson	ORP	pH	Temperature	Conductivity
ORP				
Pearson correlation	1.000	-0.188**	-0.094**	-0.045**
Sig. (2-tailed)		0.000	0.000	0.000
pH				
Pearson correlation	-0.188**	1.000	-0.335**	-0.039**
Sig. (2-tailed)	0.000		0.000	0.000
Temperature				
Pearson correlation	-0.094**	-0.335**	1.000	-0.006
Sig. (2-tailed)	0.000	0.000		0.174

Table 3: Non parametric correlations

Kendall's tau_b	ORP	pH	Temperature	Conductivity
ORP				
Correlation coefficient	1.000	-0.182**	0.056**	-0.064**
Sig. (2-tailed)	0.0	0.000	0.000	0.000
pH				
Correlation coefficient	-0.182**	1.000	-0.308**	0.033**
Sig. (2-tailed)	0.000		0.000	0.000
Temperature				
Correlation coefficient	0.056**	-0.308**	1.000	-0.004
Sig. (2-tailed)	0.000	0.000.		0.164
Conductivity				
Correlation coefficient	-0.064**	0.033**	-0.004	1.000
Sig. (2-tailed)	0.000	0.000	0.164	
Spearman's rho				
ORP				
Correlation coefficient	1.000	-0.266**	0.068**	-0.097**
Sig. (2-tailed)		0.000	0.000	0.000
pH				
Correlation coefficient	-0.266**	1.000	-0.430**	0.046**
Sig. (2-tailed)	0.000		0.000	0.000
Temperature				
Correlation coefficient	0.068**	-0.430**	1.000	-0.005
Sig. (2-tailed)	0.000	0.000		0.217
Conductivity				
Correlation coefficient	-0.097**	0.046**	-0.005	1.000
Sig. (2-tailed)	0.000	0.000	0.217	

since temperature incorporates seasonal variance. Table 5 presents results with ORP as a control variable. ORP as a control variable could disregard the

Table 4: Partial correlations with temperature as control variable

Parameters	ORP	pH	Conductivity
Temperature			
Control			
ORP			
Correlation	1.000	-0.234	-0.046
Significance (2-tailed)		0.000	0.000
DF	0	55002	55002
pH			
Correlation	-0.234	1.000	-0.043
Significance (2-tailed)	0.000		0.000
DF	55002	0	55002
Conductivity			
Correlation	-0.046	-0.043	1.000
Significance (2-tailed)	0.000	0.000	
DF	55002	55002	0

Table 5: Partial correlations with ORP as control variable

Parameters	Temperature	pH	Conductivity
ORP			
Control			
Temperature			
Correlation	1.000	-0.361	-0.010
Significance (2-tailed)		0.000	0.018
DF	0	55002	55002
pH			
Correlation	-0.361	1.000	-0.048
Significance (2-tailed)	0.000		0.000
DF	55002	0	55002
Conductivity			
Correlation	-0.010	-0.048	1.000
Significance (2-tailed)	0.018	0.000	
DF	55002	55002	0

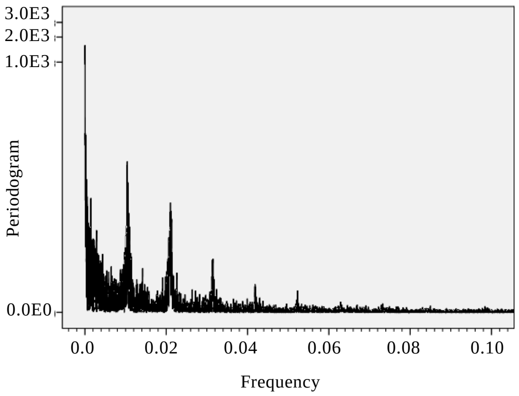

Fig. 8: A periodogram of temperature by frequency

temperature-pH association. However, the outcome of partial correlation analysis shows, Table 4-5, that all correlations remain.

Spectral analysis of the four factors reveals various periodicities. First the variable temperature exhibits a 24 h and a 12 h periodicity as main Fourier modes. It is also characterised by a less important seasonal periodicity. Fig. 8-11.

The fast Fourier analysis of the variable OPR, (Fig. 12), suggests that there is no periodic pattern on it.

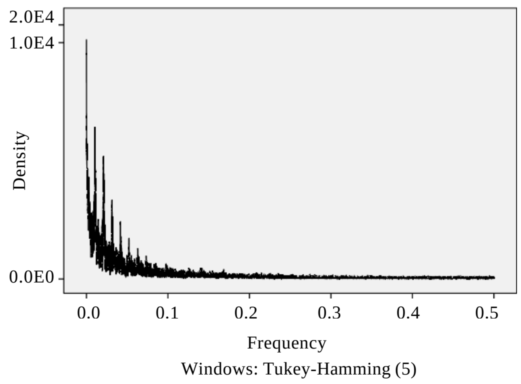

Fig. 9: Spectral density plot of temperature

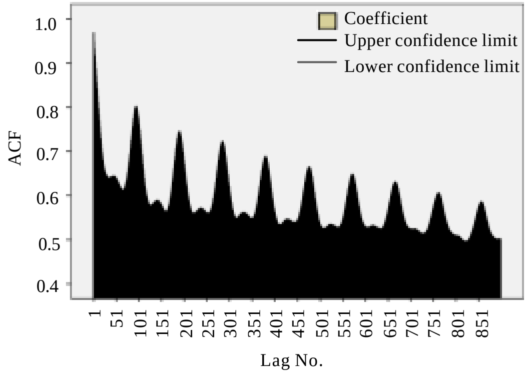

Fig. 10: Autocorrelation function plot of temperature

The same conclusion arises also from the spectral density analysis, the autocorrelation function and the partial autocorrelation function.

Spectral analysis of the variable pH exhibits a 24 h and a 7.5 days periodicity as main Fourier modes. It is also characterised by a less important seasonal periodiciry (Fig. 13-16). Finally, conductivity exhibits a not very strong 24 h periodicity as can be seen in Fig. 17-19.

The overall conclusion of the spectral analysis is that the 12 and 24 h periodicities probably are caused from sea tides. Thermopylae hot spring waters are mixed with sea water from the nearby coast. The 7.5 days periodicity found may be associated with the spring and neap tides again from the nearby sea waters entering the underground tank of water.

In the present study the physicochemical characteristic of Thermopylae natural water hot springs in Central Greece were investigated using standard methods of time series analysis. This analysis was based on data coming from

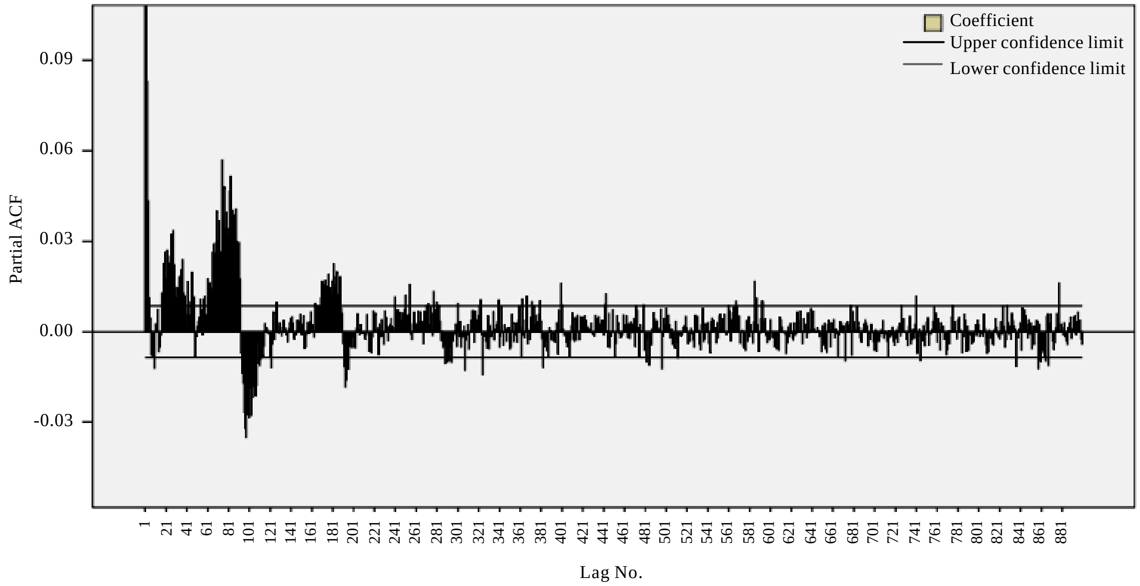

Fig. 11: Partial autocorrelation function plot of temperature

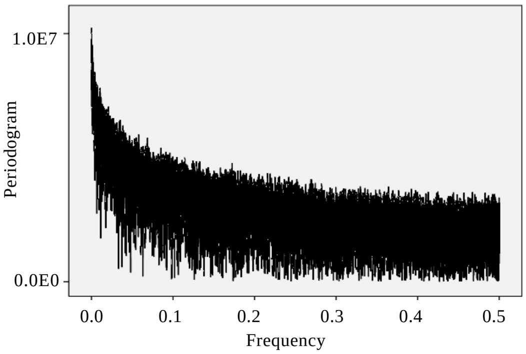

Fig. 12: Periodogram of OPR

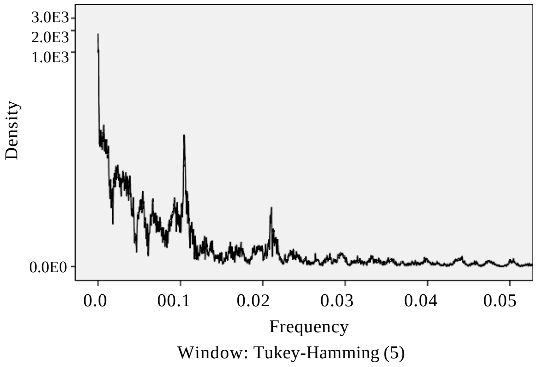

Fig. 14: Spectral density plot of pH

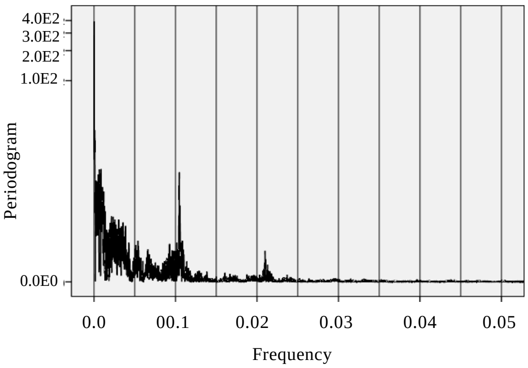

Fig. 13: Periodogram of pH

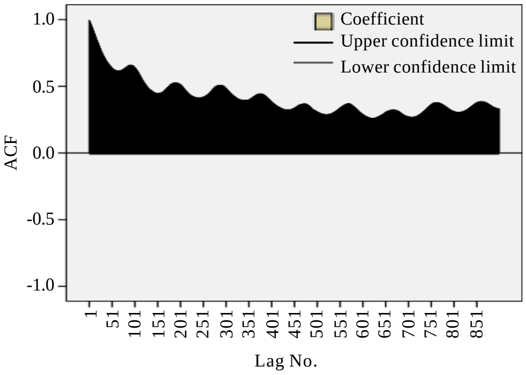

Fig. 15: Autocorrelation function plot of pH

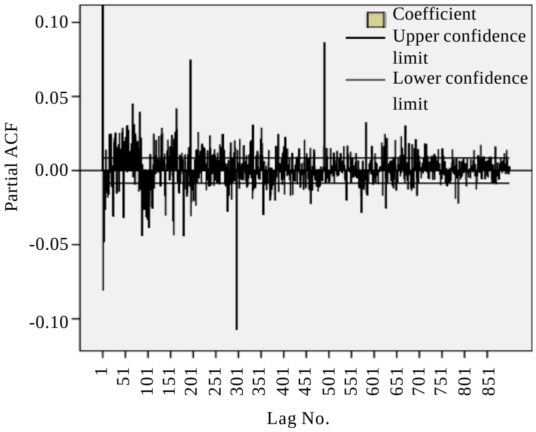

Fig . 16: Partial autocorrelation function plot of pH

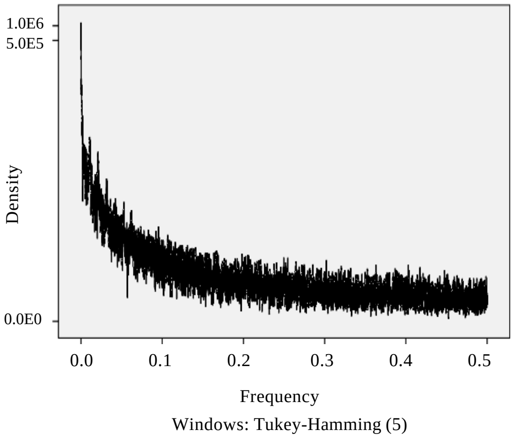

Fig. 17: Spectral density plot of conductivity

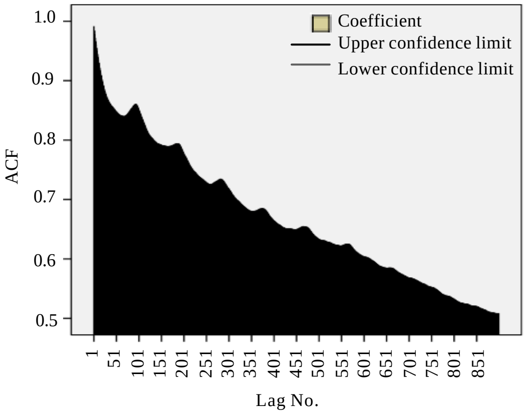

Fig. 18: Autocorrelation function plot of conductivity

on-line measurements of pH, temperature, oxidative-redox potential and conductivity.

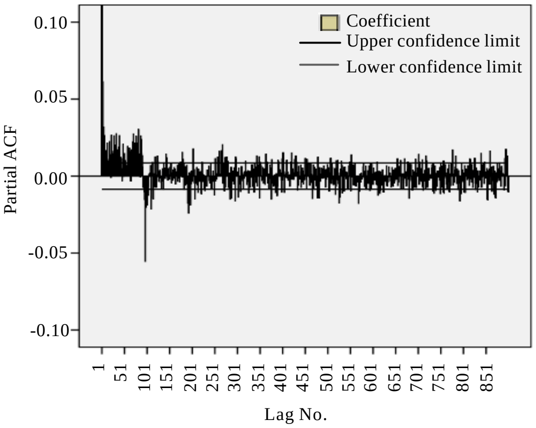

Fig. 19: Partial autocorrelation function plot of conductivity

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