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Monitoring, modeling, and assessment of water quality and quantity in River Pinios, using ARIMA models

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ABSTRACT

The purpose of this study is to analyze surface water quality and discharge data samples from River Pinios at Region of Thessaly, Central Greece. The statistical samples of each one of the variables consisted of a maximum of 188 monthly observations over a period of 16 years. For these measurements stochastic modeling algorithms were used by ARIMA Models in order to assess water quality and quantity parameters and to compare the measurements with the legislation standards. By using ARIMA to prewhiten each time series, relationships between the parameters were demonstrated. Moreover, the time response between the fluctuations of water temperature (T_w) with the ones of (1) dissolved oxygen (DO), (2) ammonium (NH_4^+), and (3) nitrates (NO_3^-) and the fluctuations of discharge (Q) with that of water electrical conductivity (ECw) was assessed. Also, (1) an evaluation of the status of river water quality according to the Hellenic and International Legislation and (2) a comparison with other corresponding studies in the area of River Pinios watershed were performed. Finally, in this study the necessity of multivariate statistical assessment of extended databases in combination with reliable and real–time monitoring data is presented, in order to "extract" information about the quality and quantity parameters and to apply managerial strategies for pollution control.

Keywords: Monitoring; Water quality assessment; Stochastic modeling; ARIMA; Prewhitening; Cross-correlation function; Water management

1. Introduction

The quality of surface water resources could significantly affect water use, especially in those areas which are downstream of a river, a natural or an artificial lake. The gradually increase of quantitative and qualitative degradation of water resources in our planet, has increased the risk of the reassurance of fresh and clean water for every purpose in our days. The main issue in water quality management is to control the pollution sources. Also, to define the good or bad quality according to the water quality standards for every use of water, as they are described in national and international laws, decrees, and directives.

The surface water quality in Greece began to be of interest since the year 1971, when the Ministry of Agricultural Development and Food (Former *Agriculture*) has started the *Program for the quality control of irrigation waters* to the major Rivers and Lakes of Greece. The next few years, six of the rivers Monitoring Stations (MS) were included in European Community Directives 77/795, 81/856, and 86/574 *About the exchange of information for the quality of surface waters in the Community* [1–3]. Other institutions, as the Ministry of Environment, Energy and Climate Change (Former *Environment, Physical Planning and Public Works*),

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the Public Power Corporation of Hellas, etc., have started to install their Monitoring Stations all over Greece.

The monitoring data can provide us with useful information, using the appropriate statistical approach. This can be performed with the use of descriptive statistics and stochastic models. The time series analysis of the water quality and quantity parameters, reveal the changes in water status during the last years. Finally, using water quality monitoring and modeling, one can locate the causes and the pollution factors, determine the control limits, and establish the principles of sustainable water management.

The research is mainly based on Modeling of time-series with ARIMA stochastic models, following the standard three steps procedure of (1) model identification, (2) model estimation, and (3) model diagnostic checking. Statistical analysis related to the estimation of cross-correlation relationships of the water quality and quantity parameters and to the estimation of the time response of specific parameters to each other and assessing the water quality and quantity parameters, taking into account the Hellenic and International Legislation and in comparison with other corresponding studies of the watershed of Pinios.

A quite important number of scientific papers are focused on issues of water quality modeling and management in water bodies in Balkan Peninsula. Argyropoulos and Ganoulis [4] studied the correlation analysis of the water quality parameters in river Axios, which is a transboundary river between FYROM and Greece. Antonopoulos et al. [5] studied River Strymon, a transboundary river between Bulgaria, Serbia, FYROM, and Greece, conducting statistical and trend analysis using the nonparametric criterion of Spearman's. Karakaya and Evrendilek [6] used monthly data of 14 years for 25 chemicals and biological and physical water properties of Big Melan Stream in Istanbul, Turkey. Then, they were separated into linear trend, seasonality, and error components using additive decomposition models. Yurekli et al. [7] presented a methodology on modelling data for monthly flows from Kelkit Stream, Turkey, using ARIMA models. Chatzinikolaou et al. [8] estimated the segments of Pinios River, which lack the retention capacity of the biological oxygen demand and nutrient input. The difference of the estimated input and output pollution loads was compared at upstream and downstream clustered areas of totally 73 segments. Psilovikos et al. [9] used 3 years daily monitoring data for River Nestos, a transboundary river between Greece and Bulgaria, in order to assess water quality and quantity issues concerning the new human impacted hydrological regime of Nestos after the construction of Thesaurus dam. Psilovikos and Sentas [10] proceeded to a comparison of the monitoring data of two stations in River Nestos, one in Nestos delta and the other in the Hellenic – Bulgarian borders targeting on integrated water resources management. Loukas [11] also used statistical and trend analysis in water quantity and quality parameters in river Pinios – Thessaly with Spearman's criterion, in order to provide a framework for sustainable water resources management. Sentas et al. [12] assessed water quality at the location of "Pagoneri," in the northern section of the flow of River Nestos with the help of statistical analysis. Psilovikos et al. [13] found that the examined network of water quality and quantity parameters in Western Macedonia lignite mines was operating properly by using statistical and trend analysis. Sentas et al. [14] developed and validated three different stochastic models on the basis of their efficiency, to forecast and their ability, to utilize auxiliary environmental information for daily dissolved oxygen (DO) data in dam-Lake Thesaurus in Greece.

In the study, research is carried out for the existence of correlation between nine parameters the River Pinios water resources, fitting ARIMA models in the primary autocorrelated data, and examining the correlation between the time-series of the residuals from the fitting of the models to each one of the initial time-series. Apart from the statistical and trend analyses, the quality of Pinios River was assessed for domestic use, aquatic life and human recreation, according the Hellenic Ministerial Decree KYA 46399/1352/1986 [1] and also International Legislation [2].

2. Material and methods

2.1. Description of study area

River Pinios watershed is located in the Region of Thessaly, Central Greece, in Water District No. 8. The watershed is surrounded by high mountains (Fig. 1). Thessaly plain is one of the most intensively cultivated and productive agricultural regions of Greece. The total area of Thessaly Region is about 13,700 km^2 and the total River Pinios watershed is 10,500 km^2, including the watershed of the Former Lake Karla of about 1,050 km^2. River Pinios springs from Pindos Mountains, flows through the mountainous relief of Pindos Mountains Chain, crosses the alluvial basin of Thessaly plain, flows eastern through the Valley of Tempi and finally discharges into the Aegean Sea after 216 km. Its main tributaries are Rivers Titarisios, Enipeas, Kalentzis, and Litheos [11].

The climate of the region is Mediterranean continental at the Western and Central side of Thessaly. The winter is cold, the summer is hot, and the temperature differs between the two seasons. In July and August temperature can reach 40°C, while in December and January 0°C or less. The average temperature is 16–17°C and the mean annual relative humidity is 67%–72%. Snowfall is very often on the mountains.

The waters of River Pinios are used primarily for irrigation. River Pinios receives the point sources of pollution due to domestic and industrial waste water and diffused nonpoint sources of runoff and agricultural return flows. The major point sources are treated and untreated urban and industrial waste water. However, the most severe problem of surface water pollution is the diffused runoff and the irrigation return flows from the cultivated lands.

The water quality parameters that are analyzed in the present study are: (1) discharge (Q, m^3 s^{-1}), (2) electrical conductivity of water (ECw, μS cm^{-1}), (3) temperature (T, °C), (4) DO (mg L^{-1}), (5) ammonium (NH_4^+, mg L^{-1}), (6) nitrates (NO_3^-, mg L^{-1}), (7) pH, (8) total phosphorus (TP, mg L^{-1}), and (9) the rate of saturated DO%. In order to analyze the above parameters, data from the Greek Ministry of Agricultural Development and Foods were used for the above purpose. The stations that have been used for the monitoring of the parameters are (1) "Gonnoi" in Tempi Railway Bridge of River Pinios and (2) "Ydatopirgos" in the Municipality of Larisa.

The station of "Gonnoi" is settled in the most representative location, focused on the pollution of the River, because all the point and nonpoint sources from agricultural and domestic uses in Pinios watershed have already been gatherred, just before it reaches the Valley of Tempi. One problem that has been occurred in "Gonnoi" Station data was the missing values in Q parameter.

These missing values were filled with data from "Ydatopirgos," which is just upstream of "Gonnoi," taking into account a linear regression analysis, assuming as independed variables the measured Q_{Ydat} values in the first Station and as depended variables the measured Q_{Gonn} values in the second one, respectively. The correlation coefficient between these measurements is $r = 0.9753$, which is assumed to be quite high.

2.2. Stochastic modeling approach used in the study

ARIMA models were developed following the standard three steps procedure described in Box et al. [15] namely model identification, model estimation, and finally, model diagnostic checking.

The form of the general linear ARIMA model with seasonality is:

$$\phi(B)\Phi(B^S)(1-B)^d(1-B^S)^D(z_t-\mu)=\theta(B)\Theta(B^S)a_t \tag{1}$$

where t the discrete time; s – the seasonality; B – the backward shift operator; M – the mean of the stochastic process, $a_t \sim N(0, \sigma_a^2)$ – the white noise; $\phi(B) = 1 - \phi_1 B - \phi_2 B^2 - \ldots - \phi_p B^p$ the nonseasonal AR operator of order p; $\Phi(B) = 1 - \Phi_1 B^s - \Phi_2 B^{2s} - \ldots - \Phi_P B^{Ps}$ the seasonal AR operator of order P; $\theta(B) = 1 - \theta_1 B - \theta_2 B^2 - \ldots - \theta_q B^q$ the nonseasonal MA operator of order q; $\Theta(B^s) = 1 - \Theta_1 B^s - \Theta_2 B^{2s} - \ldots - \Theta_Q B^{Qs}$ – the seasonal MA operator of order Q; $(1 - B)^d = \nabla^d$ – the nonseasonal deference operator of order d; and $(1 - B^s)^D = \nabla s^D$ – the seasonal deference operator of order D.

This model is expressed as ARIMA $(p,d,q)(P,D,Q)_s$ and the unknown parameters are $p + P + q + Q$ plus one more, if the mean is contained in the model.

"Gonnoi" and "Ydatopirgos" Stations, record in a monthly frequency, successively for 16 years (April of 1980–November of 1995) quantitative and qualitative parameters of the hydrologic regime of River Pinios. These monthly records constitute time series for every parameter. The best fitted ARIMA model was chosen for each parameter and it is described next. The statistical package that is used for the fitting of stochastic models is SPSS.

2.2.1. Model identification

The first step includes the identification of the type and the order of the model. The purpose of this step is to determine the order of differences required to obtain stationarity and also the order of seasonal and nonseasonal AR and MA operators for given series [15]. Stationarity is

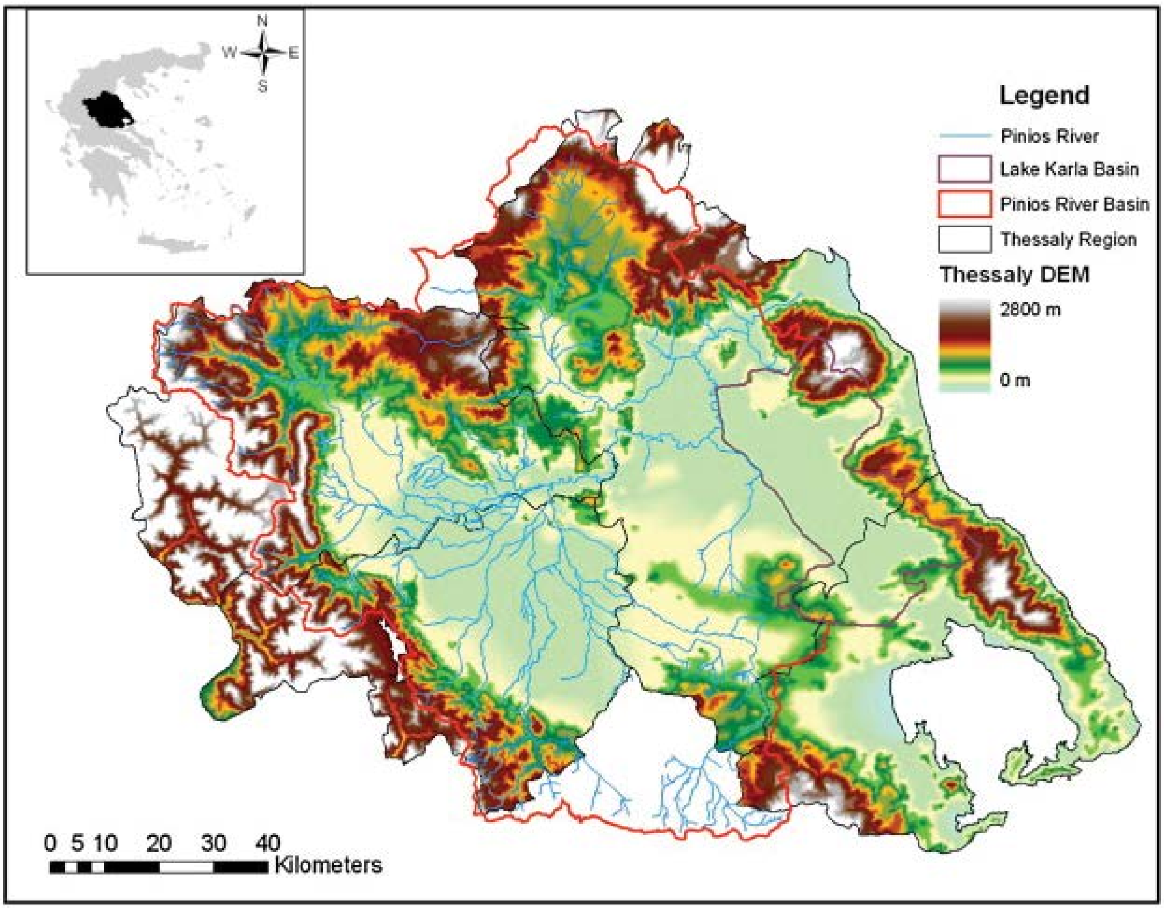

Fig. 1. Topographic map of Thessaly Region with Pinios and Karla watersheds [11].

a necessary condition in building an ARIMA model. The graphs of sample autocorrelations ACF and sample partial autocorrelations PACF help to obtain initial assumptions for the type of the model. For the seasonal ARIMA model, the identification step starts with the estimation of the seasonal model and afterwards with the analysis of its residuals. In a well-identified seasonal model, its residuals contain the non-seasonal portion of it.

2.2.2. Model estimation

The second step includes the estimation of the model parameters from the data. The parameters with significance greater than 0.05 are considered equal to zero or insignificants. For the fitting of a model the following criteria are used:

- Akaike's Information Criterion AIC [16]. The mathematical formula of this criterion is:

$$\mathrm{AIC}(k) = n \ln \hat{\sigma}_{\alpha}^{2} + 2k \tag{2}$$

where k the number of parameters in the model, n the number of observations that is equivalent to the number of residuals that can be calculated from the series, and $\hat{\sigma}_{\alpha}^{2}$ the maximum likelihood estimate of the residuals variance σ_{α}^{2}.

For an ARMA (p,q) model, $k = p + q + 1$ denotes the number of parameters estimated in the model, including a constant term.

- Schwartz's Bayesian Criterion *SBC* [17]
  The mathematical formula of this criterion is:

$$\mathrm{SBC}(k) = n \ln \hat{\sigma}_{\alpha}^{2} + k \ln n \tag{3}$$

where n, k, and $\hat{\sigma}_{\alpha}^{2}$ are defined as above.

The min value of AIC's and SBC's criteria indicate the order of the best fitted model.

2.2.3. Model diagnostic checking

In this step, the independence and the fitting to the normal distribution of the residuals are tested. For the independence of the residuals we use:

- The graph of the residuals autocorrelation function (RACF, $r_k(\hat{a})$). The autocorrelation of the residuals for every lag must be no significant.
- The Q statistic. The null hypothesis of this test is:

$$H_0 : \rho_1 = \rho_2 = \ldots = \rho_\kappa = 0$$

with the test statistic:

$$Q = n(n+2)\sum_{k=1}^{K}(n-k)^{-1} r_k^2(\hat{a}) \tag{4}$$

which is approximately distributed as X^2_{K-p-q}

$r_k(\hat{a})$ (k = 1, 2, … K) are the first K autocorrelations of the residuals and K is typically chosen in the range of 15–30.

The Kolmogorov–Smirnov test [18] and the Q–Q plot are used for the residuals fitting to the normal distribution.

2.3. Correlation analysis

In this work we carry out the usual identification and estimation methods to obtain an ARIMA model for the X_t process, which to a close approximation, transforms the autocorrelated input series x_t to the white noise series a_t (the series of the residuals). The above procedure is called prewhitening [19].

2.3.1. Pearson's correlation coefficient

The correlation coefficient represents the correlation between two different variables X and Y. The most popular is the Pearson's correlation coefficient which measures the linear correlation between variables that follow normal distribution.

The mathematical form for the sample correlation coefficient is:

$$r = \frac{S_{XY}}{S_X S_Y} \tag{5}$$

where S_{XY} the sample covariance of the variables X, Y and S_X, S_Y the standard deviations of X and Y, respectively.

2.3.2. Cross-correlation function

The cross-correlation function (CCF) is a useful indicator of strength and direction for the relation between two stationary time series. For a given set of time series data x_t and y_t, t = 1, 2, …, n, the CCF [$\rho_{XY}(k)$, k = 0, ±1, ±2, …,] is estimated by the following sample CCF.

$$r_{XY}(k) = \frac{c_{XY}(k)}{\sqrt{c_{XX}(0)c_{YY}(0)}} \tag{6}$$

$$\text{where } c_{XY}(k) = \begin{cases} \dfrac{1}{n}\displaystyle\sum_{t=1}^{n-k}(x_t - \bar{x})(y_{t+k} - \bar{y}), & k = 0,1,\ldots,(n-1) \\ \dfrac{1}{n}\displaystyle\sum_{t=1-k}^{n}(x_t - \bar{x})(x_{t+k} - \bar{y}), & k = -1,-2,\ldots,-(n-1) \end{cases} \tag{7}$$

The CCF represents the linear relation between the processes X_t and Y_{t+k} for k = 1, 2, …, n degrees of freedom.

[$\rho_{XY}(0) = \rho_0$] is the Pearson's correlation coefficient between the variables X_t and Y_t.

The CCF is not symmetric [$\rho_{XY}(k) \neq \rho_{XY}(-k)$] and it is important to examine the CCF for positive and negative lags.

Under the assumption that X_t and Y_t are uncorrelated [$r_{XY}(k) \sim N(0,1/n)$] and the null hypothesis, [$H_0 : \rho_{XY}(k) = 0$] is rejected if $\left|r_{XY}(k)\right| > z_{\alpha/2}\dfrac{1}{\sqrt{n}}$.

3. Results and discussion

3.1. Stochastic models and trend analyses

The direct – empirical check for the existence of correlations from the initial observations is not necessary because there are correlations between the observations of each parameter and requires stationarity. Therefore, we used the method of prewhitening to transform the autocorrelated input series to the white noise residual series.

The steps of the analysis were as follows:

- The best ARIMA model was chosen for each parameter.
- The residuals obtained from the model fitting were checked for independence and the goodness of fit assessment to the normal distribution.
- Finally, the Pearson's correlation coefficient between the residuals for each parameter was estimated.

The parameters with significant cross correlation (correlations with delay) present hydrological interesting and are examined.

The data of each parameter constitute a discrete time-series with a maximum of 188 observations. From this monthly data an ARIMA model is built, following the Box and Jenkins approach [20]. It was found that the parameters ECw, NO_3^-, and NH_4^+ had a constant variance and mean value and therefore were stationary. The parameters T, % DO, and TP had a period of 12 months seasonality and finally pH and DO had a significant trend. Specifically for Q, a seasonal model was fitted to the logarithm of the observations. We verified that the series residuals are corresponded to white noise for all the parameters.

The models identified for the time series of the parameters were:

- For ECw, the *ARIMA*(0,0,2) model with analytical expression

$$y_t = 464.575 + e_t + 0.512e_{t-1} + 0.303e_{t-2} \tag{8}$$

- For pH, the *ARIMA*(1,1,1) model with analytical expression

$$y_t = 1.463y_{t-1} - 0.463y_{t-2} + e_t - 0.921e_{t-1} \tag{9}$$

- For T, the *ARIMA*$(1,0,0)(0,1,1)_{12}$ model with analytical expression

$$y_t = 0.317y_{t-1} + y_{t-12} - 0.317y_{t-13} + e_t - 0.849e_{t-12} \tag{10}$$

- For DO, the *ARIMA*(1,1,0) model with analytical expression

$$y_t = 0.601y_{t-1} + 0.399y_{t-2} + e_t \tag{11}$$

- For %DO, the *ARIMA*$(1,0,1)(0,1,1)_{12}$ model with analytical expression

$$y_t = 0.801y_{t-1} + y_{t-12} - 0.801yt - 13 + e_t - 0.507e_{t-1} - 0.718e_{t-12} + 0.364e_{t-13} \tag{12}$$

- For NO_3^-, the *ARIMA*(0,0,1) model with analytical expression

$$y_t = 7.504 - 0.577\ e_{t-1} + e_t \tag{13}$$

- For NH_4^+, the *ARIMA*(0,0,1) model with analytical expression

$$y_t = 0.080 + e_t + 0.263e_{t-1} \tag{14}$$

- For TP, the *ARIMA*$(1,0,0)(1,0,1)_{12}$ model with analytical expression

$$y_t = 0.279y_{t-1} - 0.951y_{t-12} + 0.265329y_{t-13} + 0.075 + e_t + 0.916e_{t-12} \tag{15}$$

- For Q, the *ARIMA*$(2,0,0)(0,1,1)_{12}$ model with analytical expression

$$y_t = \exp\left(0.265\ln y_{t-1} + 0.182\ln y_{t-2} + \ln y_{t-12} - 0.265\ln y_{t-13} - 0.182\ln y_{t-14} + e_t - 0.767e_{t-12}\right) \tag{16}$$

In Fig. 2 the observed and the estimated monthly values after the ARIMA models, for the nine series are shown.

Table 1, shows all the 36 pair-wise correlations between the nine parameters. In each cell, the significance for the test with null hypothesis $H_0 : \rho = 0$ is recorded against the alternative hypothesis $H_1 : \rho \neq 0$ (Sig. 2–tailed). Moreover, the significant correlation coefficients at significant level 5% are noted with one asterisk and at significant level 1% with two asterisks.

The following pairs of parameters, are found positive correlated:

- ECw and pH ($r = 0.278$),
- ECw and DO ($r = 0.147$),
- ECw and NO_3^- ($r = 0.493$),
- pH and NO_3^- ($r = 0.162$),
- T and %DO ($r = 0.234$), and
- DO and %DO ($r = 0.496$) (Table 1).

The following pairs of parameters are found negative correlated:

- Q and pH ($r = -0.179$),
- Q and NH_4^+ ($r = -0.177$),
- ECw and T ($r = -0.148$), and
- T and DO ($r = -0.346$) (Table 1).

Further analysis was made to identify delayed correlation between the parameters of T with DO, NH_4^+, and NO_3^-, and Q with ECw. We investigated the cross correlation between the residuals of the above pairs (Fig. 3).

The results of the analysis are:

- T and DO are significantly negative correlated with a time delay of 2 months. This means that increase of the T results affects decrease of DO after 2 months.
- For the parameters T and NH_4^+ the CCF for lag = 12 is significantly different from zero [$\rho_{XY}(-12)^1\ 0$], so any change of T influences the values of NH_4^+ with a response of 1 year (a period which is not assumed to be reliable).
- The CCF between T and NO_3^- gave [$\rho_{XY}(5)^1\ 0$]. This means that any change of T, influences the measurements of NO_3^- after 5 months.

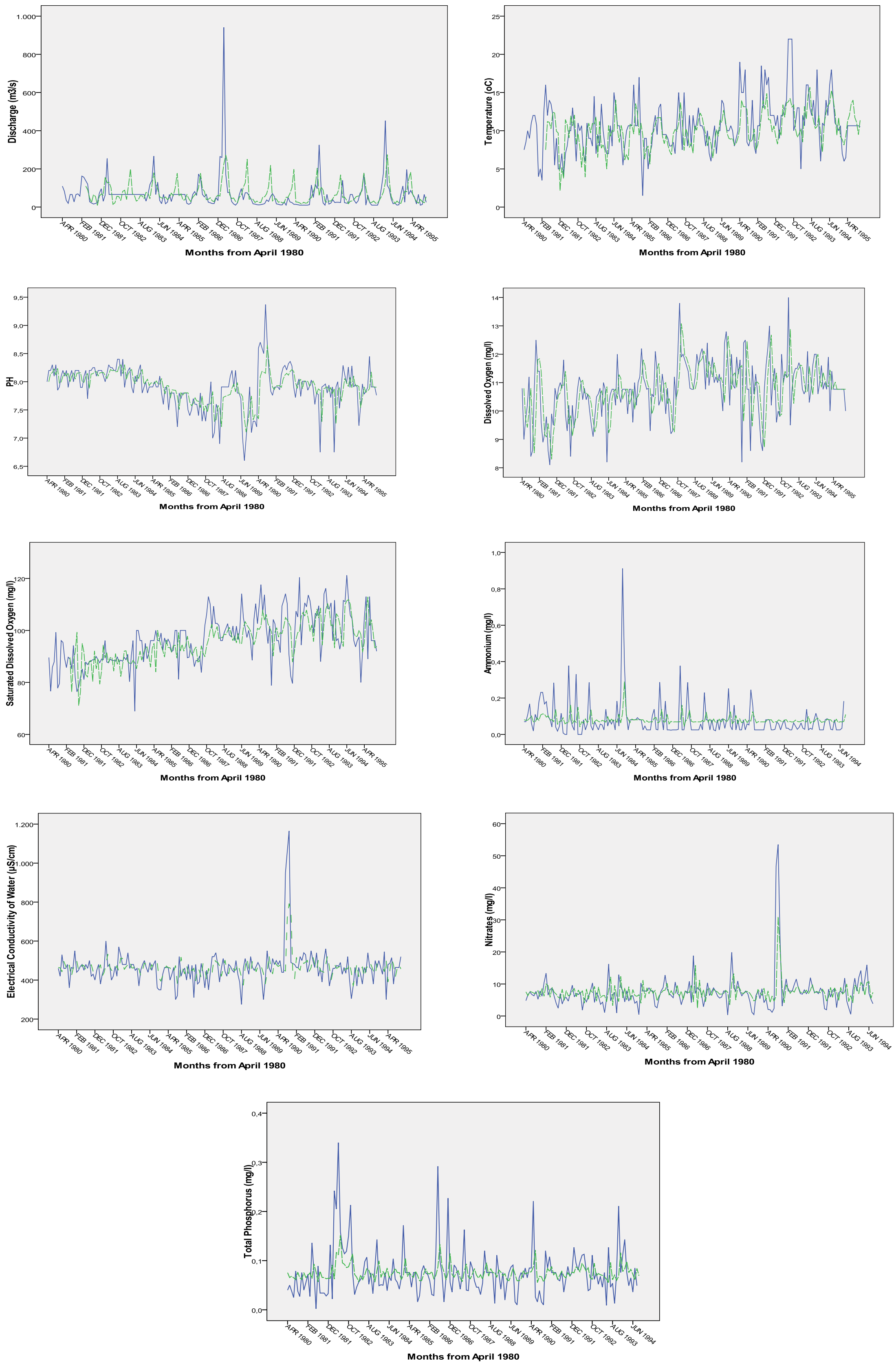

Fig. 2. The observed and the estimated (dashed line) monthly values using the *ARIMA* models, for the nine series (see text for details for the models). Continuous line the observed values and dashed line the estimated values.

Table 1
Correlation coefficient among nine parameters of River Pinios and *p*-value for significance

	Q	ECw	pH	T	DO	% DO	NO_3^-	NH_4^+	TP
Q	1	−0.035	0.179*	0.013	−0.081	−0.068	0.081	−0.177*	0.108
		0.646	0.017	0.860	0.282	0.367	0.307	0.025	0.171
ECw		1	0.278**	−0.148*	0.147*	0.016	0.493**	−0.017	−0.99
			0.000	0.049	0.044	0.837	0.000	0.821	0.195
pH			1	−0.44	0.106	0.100	0.162*	0.030	−0.114
				0.561	0.149	0.188	0.033	0.698	0.137
T				1	−0.346**	0.234**	−0.075	0.022	−0.002
					0.000	0.002	0.343	0.785	0.984
DO					1	0.496**	0.106	−0.001	−0.100
						0.000	0.168	0.992	0.193
% DO						1	−0.055	0.006	−0.044
							0.485	0.943	0.584
NO_3^-							1	−0.126	0.048
								0.099	0.531
NH_4^+								1	−0.0495
									0.520
TP									1

* denotes significant correlation coefficient at the 5% level and ** for 1% level.

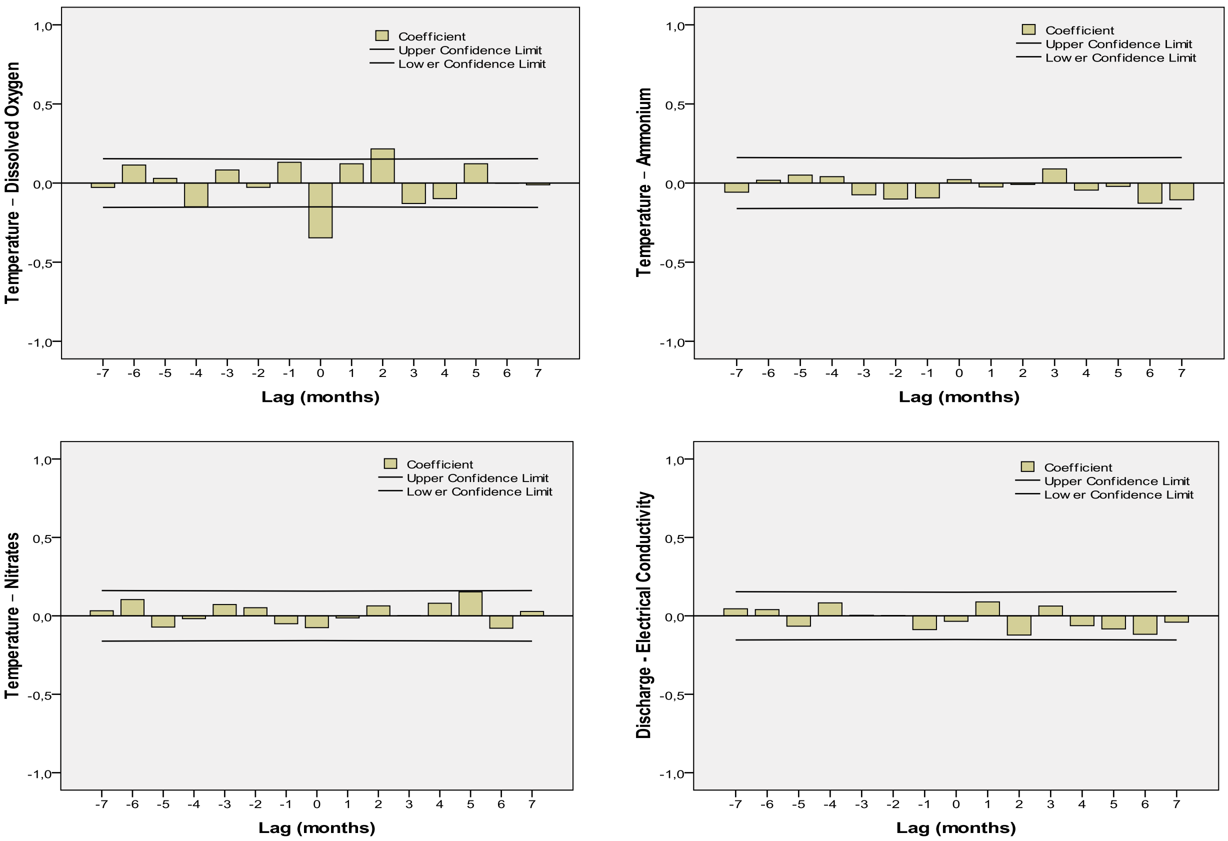

Fig. 3. The graphs of sample cross-correlation function between parameters.

- Finally, for the parameters Q and ECw, $\rho_{XY}(6)$ is marginally significant to say that any change in Q influences ECw after 6 months. Such a phenomenon has been recorded in two cases in River Nestos [9] and Agiasma Lagoon [21]. In the first case, high values of Water Level were associated with low values of ECw in Nestos fresh waters [9,22] and in the second case, high values of Water Level were associated with low values of Salinity in Agiasma Lagoon brackish waters [21], respectively. In both cases a response – delay – has been observed between the inverse peak values of the two quadratic models.

3.2. Assessment of the water quality and quantity

The "KYA 46399/1352/1986," imposed measures for the continuous monitoring, the control of the quality parameters in Pinios River and the ecological preservation of the natural environmental. The statistical analysis of the recorded parameters that were examined in this study is presented in Table 2.

3.2.1. pH

The normal range for pH to support the aquatic life is 5.5–9, while the ideal level for potable water should be between 6.5 and 8.5 [1,2]. In this station pH values were ranking from 6.60 to 9.37 and the mean value was 7.9.

The lower value of 6.6 was recorded in August 1989, and it was kept in acceptable limits. On the other hand, the higher value was recorded in August 1990, an isolated value of 9.37 which did not present serious problem to biota (Fig. 4). It was the only one though, which exceeded the maximum allowable values for both uses of potable water and aquatic life preservation. Sudden changes in pH values could be harmful or even fatal to biota, especially fish. As the pH rises, it increases the toxicity of chemicals such as ammonia. Also occasional problems could be caused by the high alkalinity of water.

3.2.2. Electrical conductivity of water – Ecw

ECw estimates the amount of total dissolved salts, or the total amount of dissolved ions in the water.

The statistical analysis of ECw time series indicated that the mean value (464.40 µS cm^{-1}) had been recorded lower than the maximum allowable value of 1,000 µS cm^{-1} according to the Hellenic Legislation for aquatic life [1]. On the other hand, it is higher than the corresponding value of 400 µS cm^{-1} according to WHO [2] for potable water. Specifically, 83% of the monitored values are higher than 400 µS cm^{-1}. The lowest values were monitored in August of 1978 and 1989 (275.00 and 300.00 µS cm^{-1}, respectively), which both did not exceed the legislations above. The highest values of ECw appear in winter period and especially in September and October of 1990 (1,165.00 and 1,060.00 µS cm^{-1}, respectively), which were higher than both the allowable limits (Fig. 5). These high values of ECw, seem to concur with low values of Q, explaining the correlation coefficient analysis that has been obtained for both parameters. A response – delay – has been observed between the inverse peaks as was mentioned above. Such phenomena has been also been observed in River Nestos Delta [9,21,24].

3.2.3. Water temperature

Water temperature measurements are ranging between 1.5°C and 22°C. The mean value is 10.65°C, where the

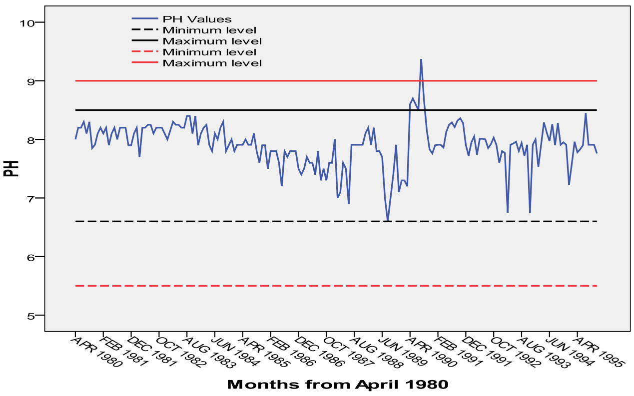

Fig. 4. The maximum and minimum allowable pH values. With red line: the minimum and maximum limits for aquatic life. With Black line: the minimum and maximum limits for potable water.

Table 2
Statistics of water quality parameters in river Pinios

Parameter	Sample size	Mean value	Median value	Max value	Min value	Standard deviation	Percentiles 25/50/75 th%
Discharge (Q, m^3 s^{-1})	188	56.015	45.985	931.51	0	88.322	10/45.98/56.01
ECw (µS cm^{-1})	188	464.40	464.40	1,165.00	275.00	94.3267	430.00/464.40/483.75
pH	188	7.9	7.9	9.37	6.6	0.3721	7.8/7.9/8.2
Water temp. (T, °C)	188	10.65	10.65	22.00	1.50	3.43	8.12/10.65/12.00
Dissolved oxygen (mg L^{-1})	188	10.7669	10.7669	14.00	8.10	1.0153	10.20/10.76/11.40
Saturated DO (%)	188	95.5707	96.0919	121.20	68.90	9.7381	88.99/96.09/102.60
Nitrates (mg L^{-1})	173	7.8112	7.1500	53.51	0.35	6.5103	5.48/7.15/8.27
Ammonium (mg L^{-1})	173	0.080	0.046	0.0912	0.000	0.099	0.025/0.046/0.080
Total phosphorus (mg L^{-1})	173	0.075	0.072	0.340	0.002	0.050	0.042/0.072/0.086

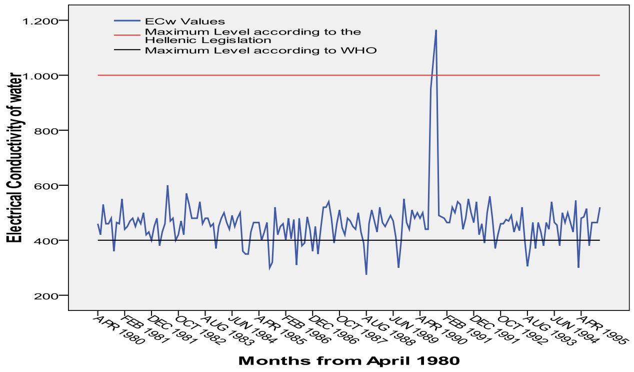

Fig. 5. The maximum and minimum allowable ECw values. With red line: the maximum level for potable water.

maximum value is recorded from July to September of 1992 (22°C) and the minimum one in October 1985 (1.5°C) (Fig. 6). From the time series analysis is assumed that the higher values appear from July to September, while the lower ones, from December to February. In the summer period the temperature values reach 10°C–15°C and in the winter period 5°C–10°C. The river water seems to keep its low temperature along its course. Both the maximum and minimum recorded values are not harmful for biota and are sufficient to support aquatic life and fall within the range of acceptable determined limits of 21.5°C for Salmonids and 28°C for Cyprinids according to the Hellenic Legislation [1]. Concerning the potable water, the values are kept in low levels.

3.2.4. Nitrates

Nitrogen-containing compounds act as nutrients in streams, rivers, and reservoirs, affecting eutrophication phenomena. The major point and nonpoint sources of nitrogen compounds into water bodies include: (1) municipal and industrial wastewater, (2) septic tanks, (3) stockbreeding activities including animals, poultry, and fish wastes, and (4) runoff from agricultural activities rich in flushing fertilizers and pesticides and urban runoff waters.

Nitrates were varied ranging from 0.35 (August 1988) to 53.51 mg L^{-1} (September 1990), with a mean value of 7.81 mg L^{-1}. According to both Hellenic Legislation [1] and WHO [2], the acceptable limits for potable water concerning on Nitrates, are between 25 and 50 mg L^{-1}. In this case, only in September 1990 (53.51 mg L^{-1}) nitrates were recorded higher than the maximum acceptable level (Fig. 7) and this was an only one isolated value. All the other monitored values are below 20 mg L^{-1}, so we can say that there is not really a hazard for aquatic life and domestic use of water, for the so far monitoring period.

3.2.5. Ammonium

Ammonium is used in fertilizers either as a compound or as ammonium salts such as sulfate and nitrate. Since ammonium is a decomposition product from urea and protein, it is found in domestic wastewater. Aquatic life and fish also contribute to ammonium levels in the aquatic environment [23].

The mean value of ammonium (0.080 mg L^{-1}) is lower than the maximum allowable values for potable water of (1) 1.5 mg L^{-1} according to the Hellenic Legislation [1] and (2) 0.5 mg L^{-1} according to WHO [2] and EU [3]. It is also lower than the maximum allowable value of 1.0 mg L^{-1} for aquatic life, according to the Hellenic Legislation [1]. Moreover the maximum value that was recorded in September 1984 (0.91 mg L^{-1}), is an isolated value just below the maximum allowable one for living conditions of fish and all the other values are below 0.4 mg L^{-1}. These values seem not to be harmful for both aquatic life and domestic use, according to both Legislations (Fig. 8).

3.2.6. Total phosphorus

Phosphorus is one of the key elements necessary for the growing of flora and fauna. Orthophosphates (PO_4^{-3}) is the most common compound formed from this element. The sum of all the chemical compounds of phosphorus, including organic and inorganic ones, constitutes the total phosphorus – TP. It is a very important parameter, because it can lead the aquatic ecosystems to eutrophication.

The mean of the monitored values of TP in Pinios was equal to 0.075 mg L^{-1} and fluctuated between a minimum value of 0.002 mg L^{-1} (June 1981) and a maximum value of 0.340 mg L^{-1} (May 1982) (Fig. 9). None of the Legislations referred to maximum allowable levels but to desirable ones.

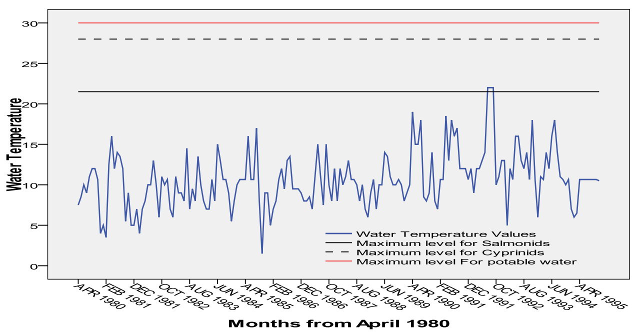

Fig. 6. The maximum and minimum allowable Tw values. With red line: The maximum level for potable water. With black line: the maximum level for aquatic life.

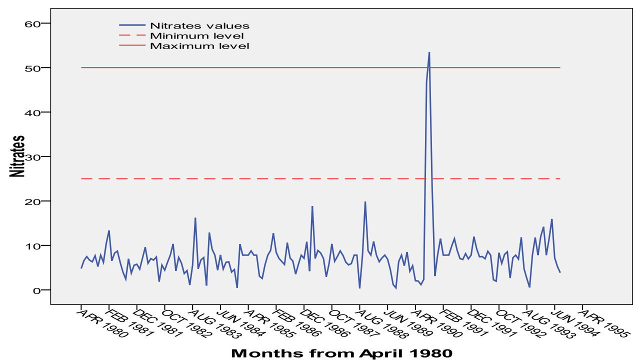

Fig. 7. The maximum and minimum allowable NO_3^- values. With the red line: the maximum level for aquatic life (continuous line) and potable water (dashed line).

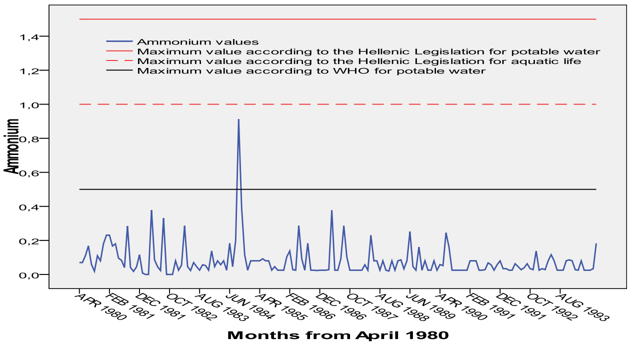

Fig. 8. The maximum and minimum allowable NH_4^+ values. With red and black line: the maximum level for potable water and aquatic life respectively.

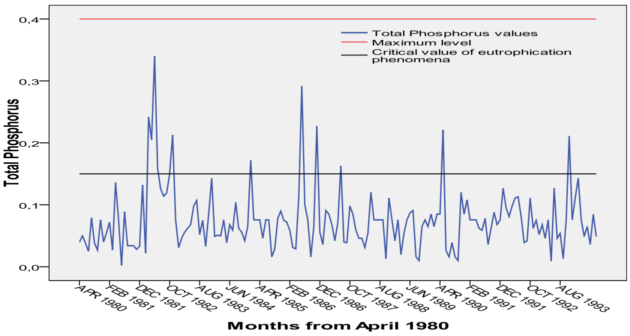

Fig. 9. The maximum and critical TP values. With red line: The desirable TP values for potable water and with black line the critical TP values for eutrophication phenomena.

So, none of the monitored values exceed the desirable level of 0.4 mg L^{-1}, that is, suggested by the Hellenic Legislation for potable water (1986). Furthermore, the mean value is lower than the critical value of eutrophication phenomena in European rivers which is considered to be 0.15 mg L^{-1} [11].

3.2.7. Dissolved oxygen

DO is a necessary and vital element to all forms of life. Adequate oxygen levels are necessary to provide aerobic life forms and natural self-purification processes in rivers and lakes. The minimum allowable level in water bodies that set aquatic life into stress is 5.0 mg L^{-1} mean daily and 4.0 mg L^{-1} minimum daily value [5]. Oxygen levels that remain below 1–2 mg L^{-1} for a few hours can result in stress and deaths of fishes.

The DO in the water was in quite satisfactory levels, all through the measured period in Pinios water. The usual range was between a minimum value of 8.1 mg L^{-1} to a maximum value of 14 mg L^{-1} (Fig. 10). Even the lower measured values are above 8 mg L^{-1} and they are considered very satisfactory to support aquatic life in Rivers Pinios and the water is definitely not suffering at all from anoxia phenomena.

3.2.8. Dissolved oxygen percentage saturation rate (%) – DO/DOsat (%)

DO percentage saturation rate is the rate of (1) the amount of measured DO in a water body – DO to (2) the potentially maximum amount of DO that could be measured in the water body – DOsat. Values between 80% and 120% were considered to be excellent and values less than 60% or over 125% were considered to be poor and harmful for the aquatic life according to Hellenic Legislation [1]. According WHO [2] for potable use, values higher than 75% are considered to be acceptable.

The recorded values were in the range of acceptable limits for aquatic life. Specifically, 94.15% of the measures

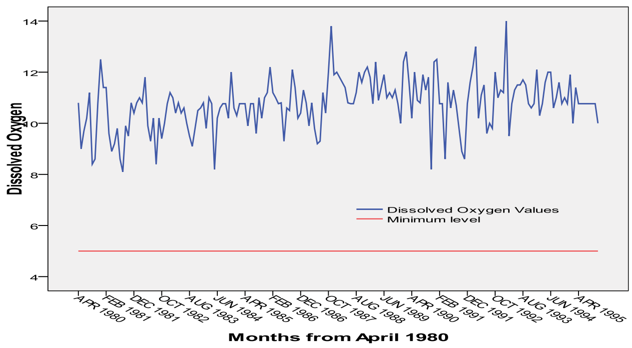

Fig. 10. The maximum and minimum allowable DO values. With red line: The critical level for aquatic life.

Table 3
Water quality criteria for potable and aquatic life, according to Hellenic and International legislation [1,2,3]

Parameter	Hellenic ministerial decree (KYA 46399/1352/1986)		International legislation (WHO, EU)
	Potable water	Aquatic life	Potable water
ECw (μS cm^{-1})	<1,000	<1,000	<400
pH	6.5 < pH < 8.5	5.5 < pH < 9	6.5 < pH < 8.5
Water temp. (T, °C)	<30	<21.5 Salmonids <28°C Cyprinids	25
Dissolved oxygen (mg L^{-1})	–	>5	–
Saturated DO (%)	80%–120%	80%–120%	>75%
Nitrates (mg L^{-1})	25–50	25–50	<50
Ammonium (mg L^{-1})	<1.5	<1	<0.5
Total phosphorus (mg L^{-1})	<0.4	<0.4	–

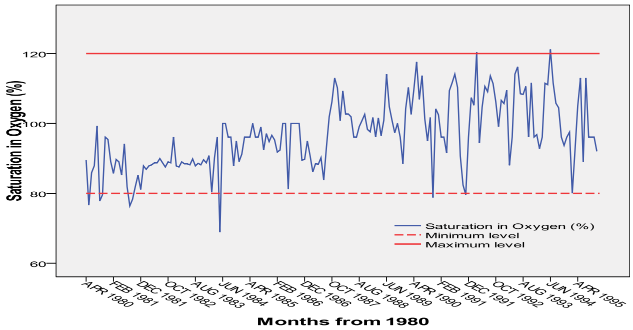

Fig. 11. The maximum and minimum allowable DO values. With red line: The maximum and minimum oxygen saturation levels (%).

are between 80% and 120%, except of some isolated values which were recorded out of the limits. The mean value was recorded equal to 95.57%, the highest value 121.20%, and the lowest 68.90% (Fig. 11). However, the water is considered to be of good quality both for potable use and aquatic life preservation.

Concerning on agricultural use of water, Loukas [11,24] estimated that the water can be used for irrigation, stockbreeding use, industrial supply, ecological use, and ecosystem sustainability taking into account WHO [2].

4. Conclusions – discussion

River Pinios is located in Thessaly region where the dominating economic activities are agriculture, tourism, stockbreeding, and fisheries. The major water uses in Thessaly are the urban water supply and the irrigation of cultivated fields. These are the main risks for pollution in the river. Especially agricultural activities are the most severe reasons of significant water quantity and quality degradation. In this study, the main three targets that have been obtained were:

- The application of stochastic modeling approach, using Autoregressive Integrated Moving Average (ARIMA) Models for the time-series of nine most important water quality and quantity parameters of River Pinios, for a period of 188 months (April 1980–November 1995). Akaike's information and Schwartz's Bayesian criteria were used to choose the best fitted ARIMA model in each one of the time-series.
- The significance of correlation was assessed for the residual series that were derived from the best fitted ARIMA models. The standard Pearson's correlation coefficient was used, combined with a prewhitening procedure to remove the effect of serial correlation. The level of significance for the correlation coefficient was 5% and 1%. For the parameters T–DO, T–NH_4^+, T–NO_3^-, and Q–ECw, cross correlation analysis were applied and time response was obtained for all the correlated pairs of the parameters. Especially for Q–ECw pair of correlation, it was found a similarity with studies on other catchments [9,21].
- The assessment of water quality and quantity parameters for River Pinios monitoring data shows that the criteria for living conditions of aquatic life and potable use, according to the Hellenic Legislation (1986), are satisfied.

In general, the monitoring data of the nine parameters were fluctuating at normal predictable levels, except of some isolated values that have no physical meaning and practically does not affect living conditions for biota and the other uses of water, as it has been obtained by analysis above. The comparison with older studies in the area of River Pinios [11,24] watershed and also International Legislation [2] indicates that for potable water use, all the parameters were below the higher allowable levels, except of the parameter of ECw, which is quite increased and 83% of the monitored values are over the higher standards of 400 µS cm^{-1}.

The analysis in the paper indicated that the quality of River Pinios water is in the range of the acceptable guideline levels, according both to Hellenic and International Legislation (Table 3) for all the uses of potable water and urban supply, aquatic life preservation, stockbreeding, and agricultural use, with an exception of the values of ECw for potable water, as according to WHO [2] and EU [3].

Further research is required on the continuous monitoring of River Pinios water resources, especially for the domestic use of water. In this direction, a fully integrated telemetric monitoring network could provide the authorities of Thessaly Region with useful data on a daily monitoring program. This could also be a powerful tool for checking the water quality status in specific water intake positions, for probable pollution episodes and it could act as an alert and decision making framework, so protecting the public health. With regards to the methodologies presented in this study, they should be extended on (1) longer time periods, (2) establishing telemetric stations, and (3) using intensive daily or even hourly monitoring data in order to apply effective management practices and strategies for implementation not only in Thessaly region, but also all over Greece.

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