Time variations of the physicochemical parameters in a Mediterranean Lake

Mentzafou A.[1*], Papadogıannı Ch.[2] And Dimitriou E.[1]

[1] Hellenic Centre for Marine Research, Institute of Marine Biological Resources and Inland Waters

46.7 km Athens - Sounio Ave., 19013, Anavissos, Attiki, Greece

[2] Agricultural University of Athens, Department of Natural Resources Management & Agricultural Engineering

Iera Odos 75, 11855, Athens, Attiki, Greece

*corresponding author:

e-mail: angment@hcmr.gr

Abstract Nowadays, water resources are under increasing pollution pressures globally. Anthropogenic activities such as intensive agriculture, industrial sprawl and urban development, together with climate change and poor water management practices, impact the ecological integrity of water bodies and lead to the deterioration of water resources quality. To mitigate these pressures, efficient monitoring efforts should be established with the use of state-of-the-art equipment that can operate in low cost and long term basis. In the particular effort, the daily physicochemical data (temperature, dissolved oxygen-DO and electric conductivity) of the period 2011-2015 from an automatic monitoring station in Koumoundourou Lake, West Attica-Greece were statistically elaborated to identify time trends that can be related to documented pollution pressures in the associated catchment.

Keywords: Koumoundourou Lake, monitoring survey, pollution pressures, statistical analysis

1. Introduction

Nowadays, water resources are under increasing qualitative and quantitative degradation globally (Wetzel, 1992). Anthropogenic modification of the natural environment due to activities such as intensive agriculture and industrial sprawl, together with population growth, climate change and poor water management practices, impact the ecological integrity of water bodies and lead to the deterioration of water resources quality, especially on fragile water bodies such as coastal lagoons and small lakes (Ruiz-Luna & Berlanga-Robles, 2003). To mitigate these pressures, a well-designed and financially supported surface water monitoring can be used, in order to understand and manage a range of stressors and societal concerns (Fölster *et al.*, 2014).

In the particular effort, state-of-the-art equipment was used in low cost and long term basis, to automatically monitor daily physicochemical data (temperature, dissolved oxygen-DO and electric conductivity) for the period 2011-2015 at Koumoundourou Lake, West Attica-Greece. The raw data were statistically elaborated, while time series analysis was performed to investigate the response of the karst system that recharges the lake. Finally, the impact of meteorological variations to physicochemical parameters of the lake was examined.

2. Study area

Koumoundourou Lake is a shallow, brackish lake lying on the north shore of Elefsina Bay, at the northeastern part of Thriassion plain in western Attica. The area of the lake is about 146,500 m^2 and the average depth is 1.0 m (Pavlidou *et al.*, 2004). A coastal embankment separates the lake from Elefsina Bay and the communication is accomplished through an artificial weir constructed in 1998 in order to increase the water level of the lake, so as to prevent the inflow of polluted groundwater (Koutsomitros *et al.*, 2001). The geological formations of the lake's catchment comprise quaternary deposits, which overly moderately karstified limestone and dolomite formations (Dimitriou *et al.*, 2012). The recharge of the lake is accomplished through karstic springs at the northeastern and southeastern part of the lake, which discharge the calcareous mountains Parnitha and Aegaleo respectively (Paraschoudis, 2002).

Due to its location near Athens and the infrastructures of the wider area (road, highway and railway networks, Elefsina port), the plain was gradually industrialized (Figure 1). The main pollution pressures in the immediate vicinity are: an oil refinery, a cement plant, industrial steel production units, fuel storage facilities and a sanitary landfill (Dimitriou *et al.*, 2012).

3. Materials and methods

3.1. *Monitoring survey*

For this effort, daily time series for the period 2011-2015 were used from the automatic telemetric station installed by Hellenic Centre for Marine Research (HCMR) - Institute of Marine Biological Resources and Inland Waters (IMBRIW) in Koumoundourou Lake (lon 23°35'60"E, lat 38°01'30"N). The instrument installed is AP-2000 Aquaprobe from Aquaread Ltd. The data are displayed online in real time (http://imbriw.hcmr.gr/en/

koumoundourou-lake-data/). The analysis concerns the investigation of three main physicochemical parameters: water temperature, dissolved oxygen (DO) and electrical conductivity.

3.2. *Statistical analysis*

In the specific effort, descriptive statistics, correlation matrixes, box-plots, frequency histograms and autocorrelogram were used in order to examine the time variations of Koumoundourou Lake's water physico-chemical parameters. Moreover, the time series analysis of physicochemical parameters and climate variables was performed using different approaches, so as to investigate the impact of meteorological variations to lake's physicochemical parameters. Under this scope correlation and autocorrelation and cross-correlation functions were employed in order to investigate the effect of precipitation to water quality and electric conductivity in particular, under the assumption that the latter is mainly impacted by discharges of underwater karstic springs.

The autocorrelation is a normalized measure of the linear correlation among successive values of the data series (Lambrakis *et al.*, 2000). Autocorrelation function (ACF) quantifies the memory effect of the system (Mangin 1984). In the second approach, the relationship between precipitation and electric conductivity was investigated. More specifically, the relationship between electric conductivity and 1 to 90 days cumulative rainfall were examined, to quantify their correlation (Pearson correlation coefficient *R*). Also, time lags from 0 to 10 days were investigated. Based on these relationships, the response of the karst system that recharges the lake was investigated, under the assumption again that the latter is mainly impacted by discharges of underwater karstic springs. Finally, in order to investigate the relationship between precipitation and electric conductivity, cross-correlation function was also used. Provided that the input stress is an uncorrelated process (white noise), such as the daily precipitation, the cross-correlogram between rainfall and electric conductivity can give information about the response of the system (Padilla & Pulido-Bosch, 1995; Larocque *et al.*, 1998). The time lag between lag 0 and the lag of the maximum value of the cross-correlation coefficient (CCF), gives an estimation of the pressure pulse transfer times through the aquifer (Panagopoulos & Lambrakis 2006).

The necessary climatological data come from Ano Liosia automatic telemetric hydrometeorological station (lon 23°40'15"E, lat 38°04'31"N; http://hoa.ntua.gr/stations/d/17/; Hydrological Observatory of Athens, operated by the Centre for Hydrology and Informatics of the National Technical University of Athens; Papathanasiou *et al.*, 2013; Figure 1). The specific station is located 8.5 km north-east of Koumoundourou Lake, and it is considered to have the most reliable and detailed time-series in the close proximity to the lake.

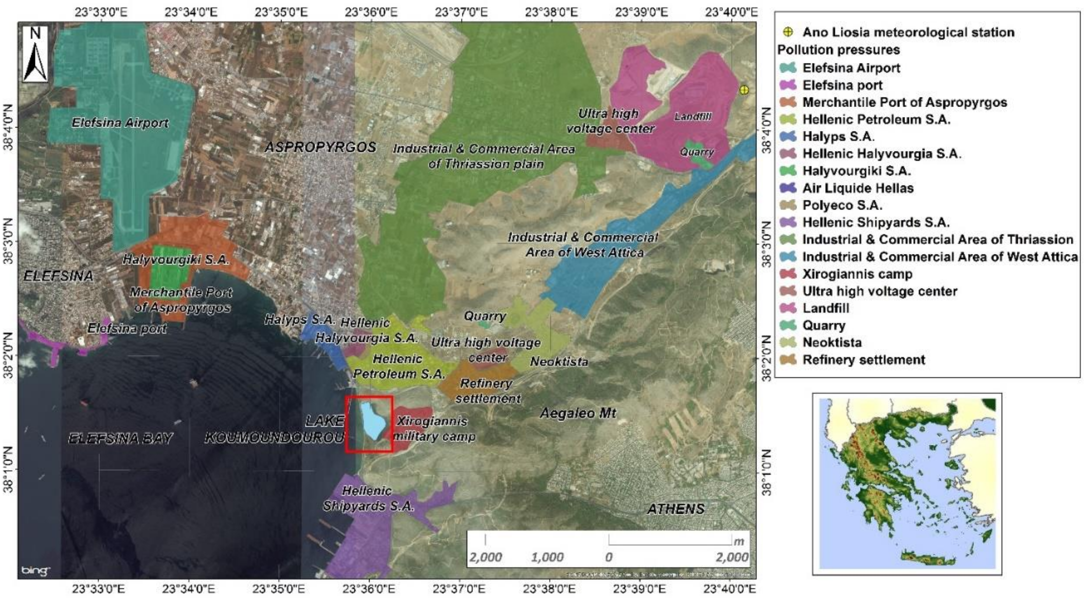

Figure 1. Aspect of the wider study area and the main pollution pressures applied

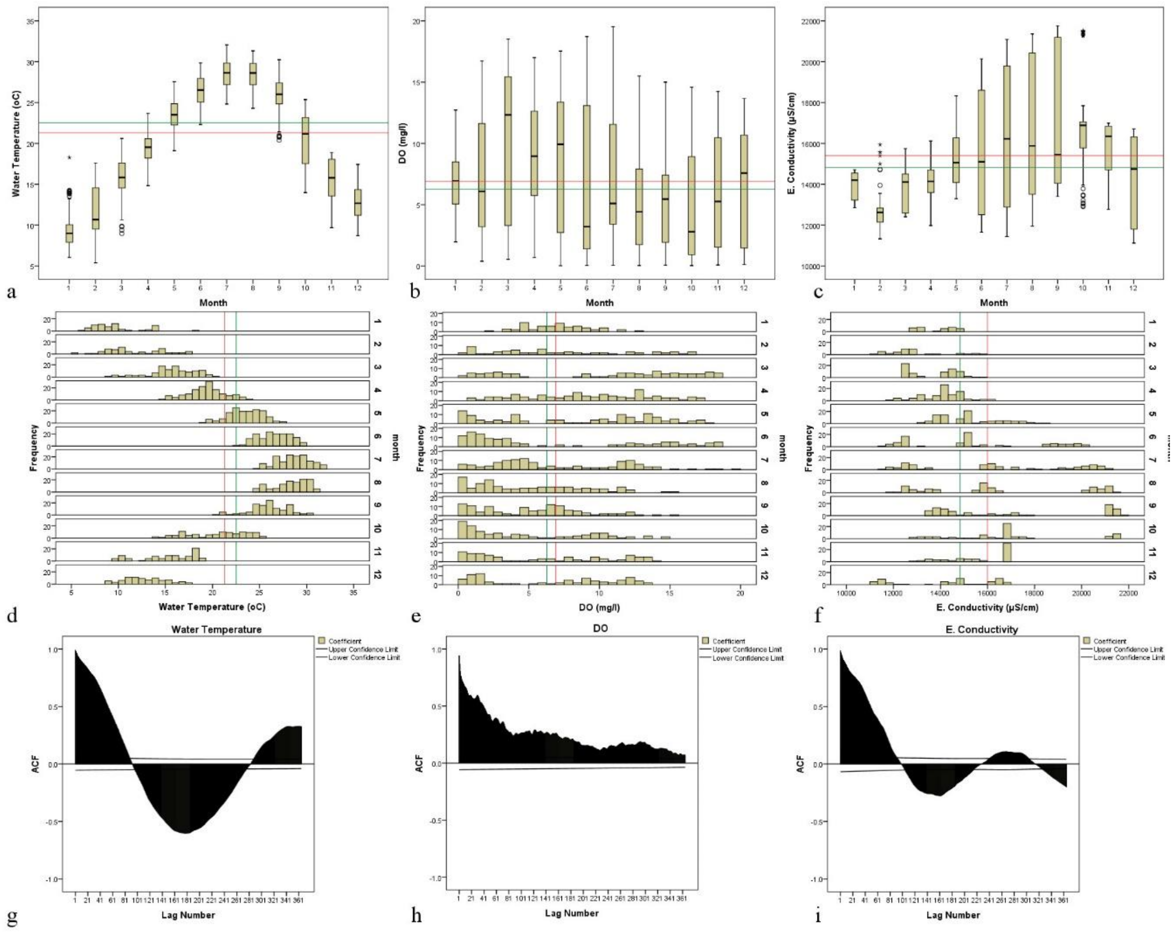

Figure 2. Monthly box-plots, monthly frequency histograms and autocorrelogram of water temperature (a, d, g), DO (b, e, h) and electric conductivity (c, f, i) of Koumoundourou Lake (red line: mean, green line: median)

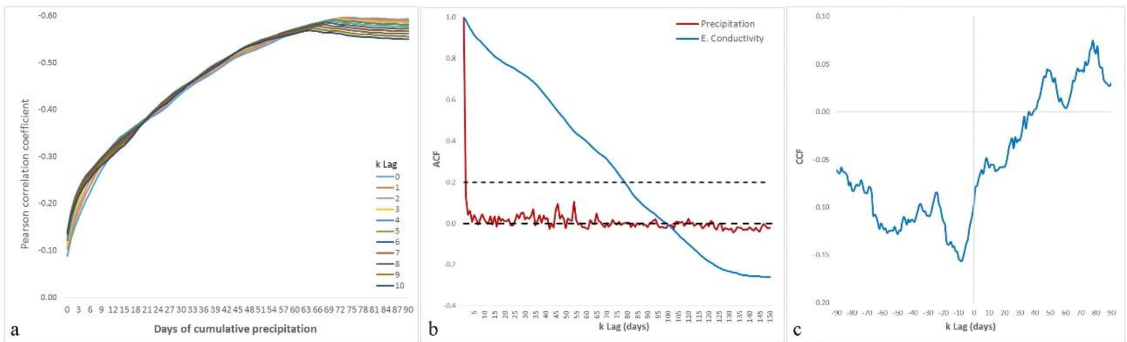

Figure 3. (a) Autocorrelogram of precipitation and electric conductivity, (b). Pearson correlation coefficient of electric conductivity and cumulative precipitation, and (c) cross- correlogram electric conductivity and precipitation

4. Results and Discussion

4.1. Descriptive statistics

Based on the statistical analysis performed in daily time-series of Koumoundourou Lake's main physicochemical parameters, the water temperature ranges between 5.38 and 32.06^{o} C, DO ranges between 0.02 and 19.52 mg/l and conductivity ranges between 11,122.62 and 21,762.87μS/cm. The median is 22.52^{o} C, 6.28 mg/l and 14,827.64 μS/ cm respectively (Figure 2).

4.2. Time variations

Based on the box-plots and frequency histograms, a seasonal variation is evident in the case of water temperature. The highest values are recorded during summer (July-August-September) and the lowest during winter (December-January-February). May to September most of the values are greater than the mean and median. Finally, the monthly variation of water temperature is small, with the exception of February and October (Figure 2a; Figure 2d). DO values remain relatively stable throughout the year with a maximum value in summer (July), when the temperature is also the highest, although these parameters are negatively correlated. This is probably due to the stronger impact that photosynthesis has on the DO levels, in relation to temperature. The biggest fluctuation is recorded during spring and summer (Figure 2b; Figure 2e). Electric conductivity shows considerable seasonal variations, since the greatest values and monthly variations are recorded during summer (June to September) and the smallest in December. These variations can be attributed to the inflows of the underwater spring that transfer freshwater in the lake and depending on the discharge level increase or lower the conductivity (Figure 2c; Figure 2f). Based on autocorrelograms there is a clear seasonal pattern with a period of one year (365 days) in water temperature and electric conductivity (Figure 2d, f). In the case of water temperature, autocorrelation shows a negative maximum at time lag 180 (in summer) and a positive maximum in lag 365 (in winter). In the case of electric conductivity, autocorrelation shows a negative maximum at time lag 170 (in summer) and 365 (in winter), and a positive maximum at time lag 270 (in autumn). DO autocorrelogram and ACF slow decrease and slow decay to zero indicate a non-stationary behaviour of the time-series (Figure 2h).

4.3. Impact of meteorological variations on lake's physicochemical parameters

Based on Figure 3a, the memory effect of electric conductivity is rather low. The autocorrelation coefficient ACF exceeds the value 0.2 after 79 days and value 0.0 after 100 days. The shape of the autocorrelation function of precipitation decreases very rapidly, the maximum ACF is 0.13 and reaches the 0.0 value in 5 days, showing that rainfall events occur randomly. Based on Figure 3b, the best correlation R (-0.596; p-value < 0.00001, significant at $p < 0.01$) was accomplished for 74 days cumulative precipitation and zero days lag. The cross-correlation function (CCF) shows a clear dissymmetry towards the positive values indicating that the precipitation influences the electric conductivity of the lake. The highest CCF of electric conductivity with precipitation is reached in 78 days (Figure 3c). Also, the maximum CCF is rather low, indicating that the input signal from precipitation is significantly reduced during its passage through the system (Larocque, 1998).

Water temperature and climate factors were in all cases statistically significantly correlated at the 0.01 level. Pearson correlation coefficient between water and air temperature at Koumoundourou Lake can be characterized as very strong (-0.954). Also, water temperature is highly correlated to net radiation (0.805), sunshine duration (0.877) and humidity (-0.759). Water temperature is moderately correlated to precipitation and wind velocity (-0.491 and 0.378 respectively). DO on the other hand was not significantly correlated at the 0.01 or 0.05 level with any climate factor. The highest correlation was achieved between DO and air temperature (-0.211). Finally, electric conductivity was moderately correlated to humidity (-0.609, p-value= 0.000216, significant at $p < 0.01$), air temperature (0.529, p-value= 0.001853, significant at $p < 0.01$), wind velocity (0.455, p-value= 0.008883, significant at $p < 0.01$), precipitation (-0.412, p-value= 0.019127, significant at $p < 0.05$) and sunshine duration (0.452, p-value= 0.009401, significant at $p < 0.05$) (Table 1).

Table 1. Correlation between Koumoundourou Lake's physicochemical parameters and climatic factors

	T (°C)	DO (mg/l)	EC (μS/ cm)
Precipitation (mm)	-.491**	-0.174	-.412*
Air temperature (°C)	.954**	-0.211	.529**
Humidity (%)	-.759**	0.074	-.609**
Net radiation (W/m^2)	.805**	-0.009	0.185
Sunshine duration	.877**	0.018	.442*
Wind velocity (m/s)	.378**	0.003	.455**

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

5. Conclusion

Based on the results, seasonal variation is evident in the case of water temperature and electric conductivity, with the highest values recorded during summer and the lowest during winter. The karstic, submerged spring plays an important role in the identified fluctuations of these parameters since depending on the seasonal variations of the springs discharge in the lake, the temperature and conductivity levels change accordingly. In low discharge periods (e.g. summer) the freshwater inflows in the lake are relatively high and this decreases electric conductivity, while in low discharge periods, sea intrusion becomes more important factor and increases the electric conductivity in the lake. The average DO values remained relatively stable throughout the year with a maximum value in summer (July), when the temperature is also the highest. This can be attributed to the high levels of photosynthesis of the aquatic algae during summer which affects more DO values than temperature.

Concerning the impact of climate factors to physicochemical parameters of Koumoundourou Lake, based on autocorrelation and cross-correlation analysis and the correlation between electric conductivity and cumulative precipitation, precipitation affects the system after 74-79 days. This is due to the broader groundwater basin that has a considerable extent and therefore the groundwater recharge and travel time to the lake creates the 2.5 months lag time. Furthermore, climate factors affect significantly the water temperature and electric conductivity of the lake. On the other hand, DO seems not to be affected by meteorological variations but mainly from biological processes. It has been reported that at urban lakes with better water quality than highly eutrophic conditions, sensitivity to variations in climatic factors was not significant owing to their better buffer capacity and regulation effect of algae growth (Wu *et al.*, 2014). Indeed, Koumoundourou Lake can be classified as mesotrophic based on OECD classification system, oligotrophic and hypertrophic based on EPA, and as of high and poor water quality based on ECOFRAME classification system (Markogianni *et al.*, 2014), while the water quality has improved and a short-term decrease of heavy metal concentrations in sediments is noted, which indicates a slow amelioration of the lake during the last decade (Mentzafou *et al*., 2016).

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