

Article

Assessment of Automatically Monitored Water Levels and Water Quality Indicators in Rivers with Different Hydromorphological Conditions and Pollution Levels in Greece

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Abstract: Water resources, especially riverine ecosystems, are globally under qualitative and quantitative degradation due to human-imposed pressures. High-temporal-resolution data obtained from automatic stations can provide insights into the processes that link catchment hydrology and streamwater chemistry. The scope of this paper was to investigate the statistical behavior of high-frequency measurements at sites with known hydromorphological and pollution pressures. For this purpose, hourly time series of water levels and key water quality indicators (temperature, electric conductivity, and dissolved oxygen concentrations) collected from four automatic monitoring stations under different hydromorphological conditions and pollution pressures were statistically elaborated. Based on the results, the hydromorphological conditions and pollution pressures of each station were confirmed to be reflected in the results of the statistical analysis performed. It was proven that the comparative use of the statistics and patterns of the water level and quality high-frequency time series could be used in the interpretation of the current site status as well as allowing the detection of possible changes. This approach can be used as a tool for the definition of thresholds, and will contribute to the design of management and restoration measures for the most impacted areas.

Keywords: automated monitoring survey; time-series statistical analysis; Greek rivers; pollution pressures; cost-effective monitoring



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1. Introduction

Access to abundant and high-quality freshwater resources has always been linked to socioeconomic development [1]. Nevertheless, freshwater is under qualitative and quantitative degradation globally due to the human-imposed pressures usually associated with this development [2]. In particular, riverine ecosystems, apart from the hydromorphological alterations imposed upon them to due to engineering interventions, are the ultimate recipients of pollution loads, related mainly to agricultural and industrial activities that take place within their watersheds [3]. In addition to these pressures, rivers are very often exposed to transient and dynamic disturbances (e.g., pollution incidents during which one or more substances are released and rapidly end up in the water column), usually from a point source [4]. Such events, especially when they occur frequently, threaten the ecological integrity of surface waters, although the consequences often cannot be thoroughly understood immediately [5].

Until recently, water quality programs for surface waterbodies were largely based on low-frequency sampling regimes that could not capture system extremes and complex hydrochemical patterns [6]. Real-time water quality and water level observations made by automatic stations provide the historical data series necessary for understanding the processes occurring between catchment hydrology and streamwater chemistry, how the time scale and flow paths of the contaminants' transport change with flow regimes and

their responses during hydrological episodes [7], and with impacts from anthropogenic activities [8]; additionally, they can be essential in determining the current site status and making short-term predictions concerning water availability and possible related risks [9]. High-temporal-resolution data are especially valuable in small-sized river catchments, in which the response to processes is high and fast [10], in understanding the mechanisms controlling pollutant diffusion caused by rainfall events [11,12] and for the detection of climate change impacts on water quality [13]. Finally, automatic monitoring systems provide real-time, continuous, reliable, and low-cost measurements [14] that enable immediate awareness of the impacts of human activities, covering both short-term (e.g., in a case of pollutant leakage [15]) and long-term events (e.g., in cases of land-use change [16]).

Currently, the existing national river monitoring network in Greece is mostly based on in situ observations taken at seasonal or monthly frequencies, and is focused on assessments of the ecological status of water bodies, as dictated by the Water Framework Directive 2000/60/EC [17]. Therefore, the main objective of the current monitoring network is the design and evaluation of water management and restoration measures on a long-term basis, but this network cannot meet the urgent need for operational, real-time monitoring of water resources at the national level [9].

Within this scope, two projects were assigned to the Hellenic Centre for Marine Research (HCMR), Department of Inland Waters. The first one, named HIMIOFoTS (Hellenic Integrated Marine–Inland Waters Observing Forecasting and Offshore Technology System; <https://www.himiofots.gr/>, accessed on 28 April 2021), aims to provide open access to data from marine and inland water monitoring networks and from forecast-related products. The inland waters component of HIMIOFoT OpenHi (Open Hydrosystem Information Network; <https://openhi.net/en/>) is national e-infrastructure for the collection, management, and dissemination of hydrological and environmental information for Greek inland water resources. The second project, named Open ELIoT (Open Internet of Things Infrastructure for Online Environmental Services; <https://www.openeliot.com/>, accessed on 28 April 2021), has the aim of implementing an integrated and economically viable Internet of Things (IoT) solution for monitoring and analyzing environmental parameters with regard to surface water. The analysis and processing of the datasets provided by the automatic monitoring stations installed under the above-mentioned projects is the next step toward the full exploitation of the infrastructure's potential.

The aim of this paper was to examine the statistical behavior of high-frequency measurements of water level and key water quality indicators at sites with known hydromorphological conditions and pollution pressures. This approach enables direct and accurate interpretation of the current status of the monitoring stations, but also allows for the detection of possible changes related to phenomena that require immediate responses, such as floods, droughts, and water pollution. Therefore, the results of this analysis will allow the definition of thresholds for similar sites, which in future can be incorporated into the automated monitoring system of surface water bodies in Greece and used as an early warning system.

For this purpose, hourly time series of water level and key water quality indicators (temperature, electric conductivity (EC), and dissolved oxygen (DO) concentration) collected from four automatic monitoring stations under different hydromorphological conditions and pollution pressures were statistically elaborated. Descriptive statistics, box plots, correlation matrixes, frequency histograms, cross-correlation analysis, and rescaled adjusted partial sums (RAPS) were employed. The above-mentioned analysis was performed on datasets derived from four monitoring sites with well-known hydromorphological status and pollution pressures. Two automated monitoring sites were located in the Pinios River in Thessaly (Nomi and Tempi), the second most productive agricultural area in Greece (for the year 2016 [18]), and two in urban environments (Lithaios and Pikrodafni). One site from each group was under pollution pressures (Nomi and Pikrodafni), while the other was considered to be less impacted by human activities (Tempi and Lithaios).

2. Materials and Methods

2.1. Sites Description

The location of the four monitoring sites is shown in Figure 1a, while the main characteristics of the corresponding catchments are presented in Table 1. Three of the four monitoring stations are located at the Pinios catchment in Thessaly, Greece while the hydromorphological conditions and the pollution pressures applied to each one of them are completely different. The monitoring stations presented in this study are part of the automatic monitoring network of the Hellenic Center for Marine Research (HCMR), Department of Inland Waters, and have been installed through Open ELIoT and HimiofoTS National projects (<https://www.openeliot.com/>, accessed on 28 April 2021 and <https://www.himiofots.gr/>, accessed on 28 April 2021).

Table 1. Summary of the characteristics of monitoring sites.

Station	Latitude	Longitude	Elevation (m)	Mean Annual Runoff (hm ³ /y)	Upstream Basin (km ²)	Dominant Land Use of Basin	Research Project	Website
Nomi	39.5266	21.9383	93	1398.5	2243	Agricultural	HIMIOFoTS	https://hydro-stations.hcmr.gr/nomi-station-pineios-river/ , accessed on 28 April 2021
Tempi	39.8968	22.6152	7	3116.1	10,897	Agricultural	HIMIOFoTS	https://hydro-stations.hcmr.gr/tempi-station-pineios-river/ , accessed on 28 April 2021
Lithaios	39.5523	21.7707	109	85.1	226	Urban	Open ELIoT	https://hydro-stations.hcmr.gr/lithaios-station/ , accessed on 28 April 2021
Pikrodafni	37.9184	23.7023	5	5.0	21	Urban	Open ELIoT	https://hydro-stations.hcmr.gr/pikrodafni-station/ , accessed on 28 April 2021

Nomi and Tempri monitoring stations have been installed at the Pinios River in Thessaly, Greece. Nomi Station is located upstream (Figure 1b). The ecological status of this specific water body (EL0816R000200039N) has been characterized as moderate and the chemical status as good, while the pressures due to abstraction for irrigation are low [19]. The possibility of the Nomi surface water body (EL0816R000200039N) to meet the environmental goals of the EU Water Framework Directive, 2000/60/EC [20] is most likely at risk [21].

Tempri monitoring station is located in the downstream part of the Pinios River, close to its mouth to the Aegean Sea, and about 120 km downstream of Nomi Station. The ecological and chemical status of the specific water body (EL0816R000200003N) has been characterized as good, while the pressure due to abstraction for irrigation is low [19].

Lithaios Station has been installed at the homonymous tributary of the Pinios River in the center of Trikala city (Figure 1c). The Lithaios River originates in Mount Antihassia and, following a northwestern–southeastern direction, flows through the city of Trikala and finally discharges into the Pinios River. The part of the Lithaios River examined that flows through the city of Trikala (EL0816R000210045H) has been subjected to water flow regulations and modifications for flood protection of the city [21] and water abstractions for irrigation (moderate pressure) [19], and has been characterized as a heavily modified water body [19]. The ecological status of the specific part of the Lithaios water body (EL0816R000210045H) has been characterized as moderate [19].

The Pikrodafni Stream is located in southeastern Attica, Greece (Figure 1d), and is one of the few remaining surface urban waterways in the wider metropolitan area of Athens. A large part of the stream is embedded as a canal. The main pollution pressures are uncontrolled urban constructions along the whole riparian zone, illegal waste disposal, sewage pipelines, and human interventions on the streambed. The stream is very often

subjected to pollution incidents and dynamic disturbances related to illegal sewage and industrial waste disposal [22]. Based on the updated River Basin Management Plans, the stream is subjected to multiple pollution pressures related to priority substances and other pollutants. The ecological status of the specific water body (EL0626R000300013N) has been characterized as moderate and the chemical status as good [23]. Nevertheless, based on a recent, thorough study, the water quality downstream was degraded, and was characterized as bad (based on nitrate concentrations), while the total physicochemical status of the stream was characterized as moderate and poor [24].

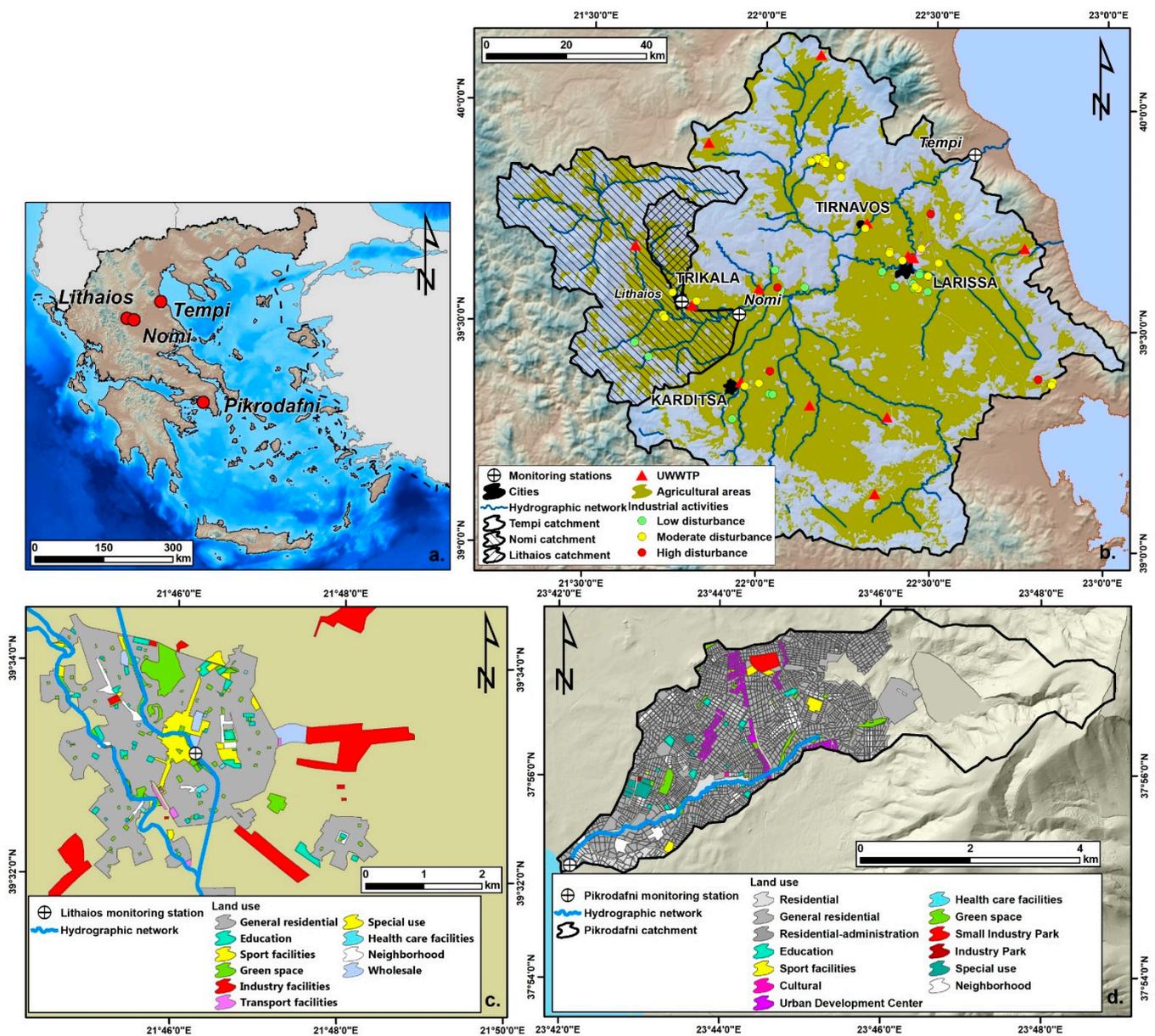


Figure 1. (a) Location of monitoring stations; (b) pollution pressure map of the Lithaios, Nomi, and Tempi catchments (industrial activities based on the General Secretariat for Industry (GSI), Hellenic Ministry of Economy and Development [25], classified based on the expected disturbances on the surrounding environment [9]); (c) pollution pressure map of the Lithaios catchment ([26], after modifications); and (d) pollution pressure map of the Pikrodafni catchment ([27], after modifications).

2.2. Monitoring Program

For the present study, hourly time series covering the hydrological year 2019/2020 from the four above-mentioned telemetric stations were employed. The time series of the

telemetric stations are automatically stored on an FTP server, while graphical visualization of the dataset is available online in real time (Table 1).

In the current study, the main water quality indicators monitored were water temperature, electrical conductivity, dissolved oxygen, and water level. These variables were chosen based on financial and maintenance limitations, but also after taking into consideration the fact that temperature and dissolved oxygen, along with discharge, are primary regulators of life in flowing waters, and extreme variations of these set the physiological and behavioral boundaries tolerated by the biota [28]. Due to the lack of stage–discharge rating curves of the monitoring sites, it was not possible to convert water level to discharge. Nevertheless, water level time-series can provide insights into the hydrological regimes of rivers [29] when discharge information is unavailable, and are often used instead of discharge in the analysis of anthropogenic activities and land use impacts on the water quality of rivers [30–32].

Before proceeding to the statistical analysis of the current database, quality assurance and control was conducted following the common practice proposed by the World Meteorological Organization [33]. Data screening and processing operations were performed by checking the data against specified screening criteria, such as the allowable variable ranges, historical maxima or minima, allowable rates of change, comparison with measurements conducted by different instruments, etc.

Finally, in the present study, categorization of the water quality status regarding the dissolved oxygen concentrations was based on the Norway classifications (<2 mg/L: Bad, 2–4 mg/L: Poor, 4–6.4 mg/L: Moderate, 6.4–9 mg/L: Good, >9 mg/L: High [34]), which are also used for the characterization of surface water bodies under the National Monitoring of the Water Status in Greece [35].

2.3. Time Series Statistical Analysis

The statistical tools employed to examine the time variations of water level and the main water quality indicators (water temperature, dissolved oxygen and electrical conductivity) of the selected monitoring stations were descriptive statistics, boxplots, correlation matrixes, and frequency histograms. The analysis was performed hourly and on a seasonal basis (winter: D–J–F, spring: M–A–M, summer: J–J–A, autumn: S–O–N).

Additionally, cross-correlation analysis and cross-correlograms were used to investigate the interactions between water level and main water quality indicators (water temperature, dissolved oxygen, and electrical conductivity), in order to determine the extent to which two data series exhibited oscillations, differing by a distance of k units in time [36]. The time lag between lag 0 and the lag of the maximum value of the cross-correlation coefficient (CCF) gives an estimation of the response of the system against a unitary impulse [37]. This statistical approach is often used in ecology, where variation in one variable is often interpreted in terms of variation in others to provide an insight of the system's response to external disturbances [36,38–40].

Cross-correlation function $r_{xy}(k)$ can be defined as:

$$r_{xy}(k) = \frac{C_{xy}(k)}{\sigma_x \sigma_y}, \quad C_{xy}(k) = \frac{1}{n} \sum_{t=1}^{n-k} (x_t - \bar{x})(y_{t+k} - \bar{y}) \quad (1)$$

where $C_{xy}(k)$ is the cross-correlogram, and σ_x and σ_y are the standard deviations of the time-series. The overbar represents the temporal mean value of the signal [41].

Finally, the rescaled adjusted partial sums (RAPS) were used to detect and quantify the trends, shifts, data clustering, irregular fluctuations, and periodicities in the record in time-series [42]. The specific approach was successfully applied in the analysis of hydrological, meteorological, and water quality indicators [43–48]. The RAPS method is based on the analysis of the time distribution of the outflow of the summary deviation curve and is expressed as [49]:

$$S_k^{**} = \frac{S_k^*}{D_x} = \frac{\sum_{t=1}^k (x_t - \bar{x})}{D_x}, \quad k = 1, 2, \dots, n \quad (2)$$

where S_k^{**} is the rescaled adjusted partial sums (RAPS), S_k^* is the adjusted partial sums or cumulative deviations from the mean, D_x is the sample standard deviation of the mean, x_t is the value of the analyzed parameter of the considered time step t , and \bar{x} is the mean of the series.

3. Results

3.1. Descriptive Statistics

The number of valid measurements per examined parameter for the hydrological year 2019/2020 was about 8400 in the case of Tempi and Pikrodafni Stations, and about 7000 and 7400 in the cases of Lithaios and Nomi Stations, respectively (Tables 2 and 3).

The maximum values and the ranges of water temperature were higher in the case of Nomi and Pikrodafni (5.7 to 31.3 °C and 7.5 to 29.0 °C in Nomi and Pikrodafni Stations, respectively) compared to Tempi and Lithaios (7.5 to 23.1 °C and 8.4 to 23.1 °C in Tempi and Lithaios Stations, respectively).

The minimum dissolved oxygen (DO) hourly concentration of Tempi Station was 5.0 mg/L and the maximum was 11.7 mg/L, whereas the mean and median concentrations were 9.3 mg/L. Based on the results, water status in Tempi Station concerning DO concentrations can be characterized as high for 66.0% of the measurements (DO concentration higher than 9 mg/L), while only a few measurements were classified as moderate (0.4%, DO concentration between 5.0 and 6.0 mg/L), and the remaining 33.6% were good (Table 2; Figure 2a,e). At Nomi Station, DO hourly concentration ranged between 0.0 and 22.9 mg/L, while the mean concentration was close to the median (5.8 and 5.9 mg/L, respectively). Water quality status concerning DO concentrations could be characterized as high or moderate in the majority of the measurements. Nevertheless, about 27% of the measurements were below moderate status (Table 2; Figure 2b,e). Although DO hourly concentrations of Pikrodafni Station varied considerably between 0.0 and 21.1 mg/L, the mean concentration was 2.0 mg/L (median 0.7 mg/L), while 75% of the measurements were lower than 3.2 mg/L. Almost 80% of the measurements were below 6.4 mg/L, indicating below-moderate water quality status (Table 3; Figure 2d,e). In contrast, the DO concentration of Lithaios Station varied between 0.0 and 14.6 mg/L, the mean and median concentrations were 7.0 mg/L, and 75% of the measurements were higher than 5.6 mg/L. About 27% of the measurements were classified as high-quality status, 47% as good, while 26% were below moderate (Table 3; Figure 2c,e).

Table 2. Descriptive statistics and correlation matrix for Tempi and Nomi Stations.

Parameter		Temperature (°C)	DO (mg/L)	E. Conductivity (µS/cm)	Water Depth (m)	Temperature (°C)	DO (mg/L)	E. Conductivity (µS/cm)	Water Depth (m)
Descriptive statistics		Tempi				Nomi			
N	Valid	8426	8426	8426	8226	7415	6590	7415	7395
	Missing	362	362	362	562	1373	2198	1373	1393
	Mean	15.4	9.3	591.0	0.50	17.1	5.8	540.1	0.45
	Median	16.0	9.3	619.4	0.33	16.8	5.9	542.5	0.25
	Std. Deviation	3.7	1.0	143.0	0.59	6.6	4.4	166.3	0.68
	Variance	13.5	1.0	20,461.9	0.35	43.2	19.3	27,668.7	0.46
	Skewness	−0.3	−0.2	−0.7	4.04	0.1	0.5	−1.3	3.88
	Minimum	7.5	5.0	146.4	0.00	5.7	0.0	56.9	0.00
	Maximum	23.1	11.7	855.8	4.38	31.3	22.9	875.3	4.40
Percentiles	25	12.0	8.6	536.8	0.23	11.2	1.7	477.1	0.18
	50	16.0	9.3	619.4	0.33	16.8	5.9	542.5	0.25
	75	18.4	9.9	697.3	0.54	23.0	8.6	654.8	0.42
Correlations									
Temperature (°C)	R	1	−0.785 **	0.184 **	−0.087 **	1	0.245 **	0.388 **	−0.338 **
	Sig. (2-tailed)		0.000	0.000	0.000		0.000	0.000	0.000
	N	8426	8426	8426	8226	7415	6590	7415	7395
DO (mg/L)	R	−0.785 **	1	−0.244 **	0.157 **	0.245 **	1	0.286 **	−0.137 **
	Sig. (2-tailed)	0.000		0.000	0.000	0.000		0.000	0.000
	N	8426	8426	8426	8226	6590	6590	6590	6570
E. Conductivity (µS/cm)	R	0.184 **	−0.244 **	1	−0.496 **	0.388 **	0.286 **	1	−0.061 **
	Sig. (2-tailed)	0.000	0.000		0.000	0.000	0.000		0.000
	N	8426	8426	8426	8226	7415	6590	7415	7395
Water depth (m)	R	−0.087 **	0.157 **	−0.496 **	1	−0.338 **	−0.137 **	−0.061 **	1
	Sig. (2-tailed)	0.000	0.000	0.000		0.000	0.000	0.000	
	N	8226	8226	8226	8226	7395	6570	7395	7395

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

Table 3. Descriptive statistics and correlation matrix for Lithaios and Pikrodafni Stations.

Parameter		Temperature (°C)	DO (mg/L)	E. Conductivity (μS/cm)	Water Depth (m)	Temperature (°C)	DO (mg/L)	E. Conductivity (μS/cm)	Water Depth (m)
Descriptive statistics		Lithaios				Pikrodafni			
N	Valid	6946	6721	6946	6946	8418	8418	8418	8496
	Missing	1842	2067	1842	1842	370	370	370	292
Mean		16.3	7.0	565.3	0.47	18.6	2.0	809.3	0.17
Median		16.5	7.0	551.2	0.41	18.4	0.7	860.1	0.17
Std. Deviation		2.6	2.4	71.7	0.16	4.9	2.9	247.4	0.05
Variance		6.5	5.6	5142.7	0.03	24.2	8.5	61,220.9	0.00
Skewness		−0.2	0.0	0.9	4.73	0.0	2.2	0.0	10.24
Minimum		8.4	0.0	209.0	0.31	7.5	0.0	66.9	0.2
Maximum		23.1	14.6	880.8	2.11	29.0	21.1	1696.3	1.15
Percentiles	25	14.3	5.6	528.5	0.39	14.2	0.0	625.2	0.16
	50	16.5	7.0	551.2	0.41	18.4	0.7	860.1	0.17
	75	18.3	8.5	591.9	0.48	23.1	3.2	996.3	0.17
Correlations									
Temperature (°C)	R	1	−0.097 **	−0.186 **	−0.343 **	1	0.390 **	0.341 **	−0.180 **
	Sig.(2-tailed)		0.000	0.000	0.000		0.000	0.000	0.000
	N	6946	6721	6946	6946	8418	8418	8418	8418
DO (mg/L)	R	−0.097 **	χ1	−0.351 **	0.109 **	0.390 **	1	0.189 **	0.094 **
	Sig.(2-tailed)	0.000		0.000	0.000	0.000		0.000	0.000
	N	6721	6721	6721	6721	8418	8418	8418	8418
E. Conductivity (μS/cm)	R	−0.186 **	−0.351 **	1	−0.206 **	0.341 **	0.189 **	1	−0.368 **
	Sig.(2-tailed)	0.000	0.000		0.000	0.000	0.000		0.000
	N	6946	6721	6946	6946	8418	8418	8418	8418
Water depth (m)	R	−0.343 **	0.109 **	−0.206 **	1	−0.180 **	0.094 **	−0.368 **	1
	Sig.(2-tailed)	0.000	0.000	0.000		0.000	0.000	0.000	
	N	6946	6721	6946	6946	8418	8418	8418	8496

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

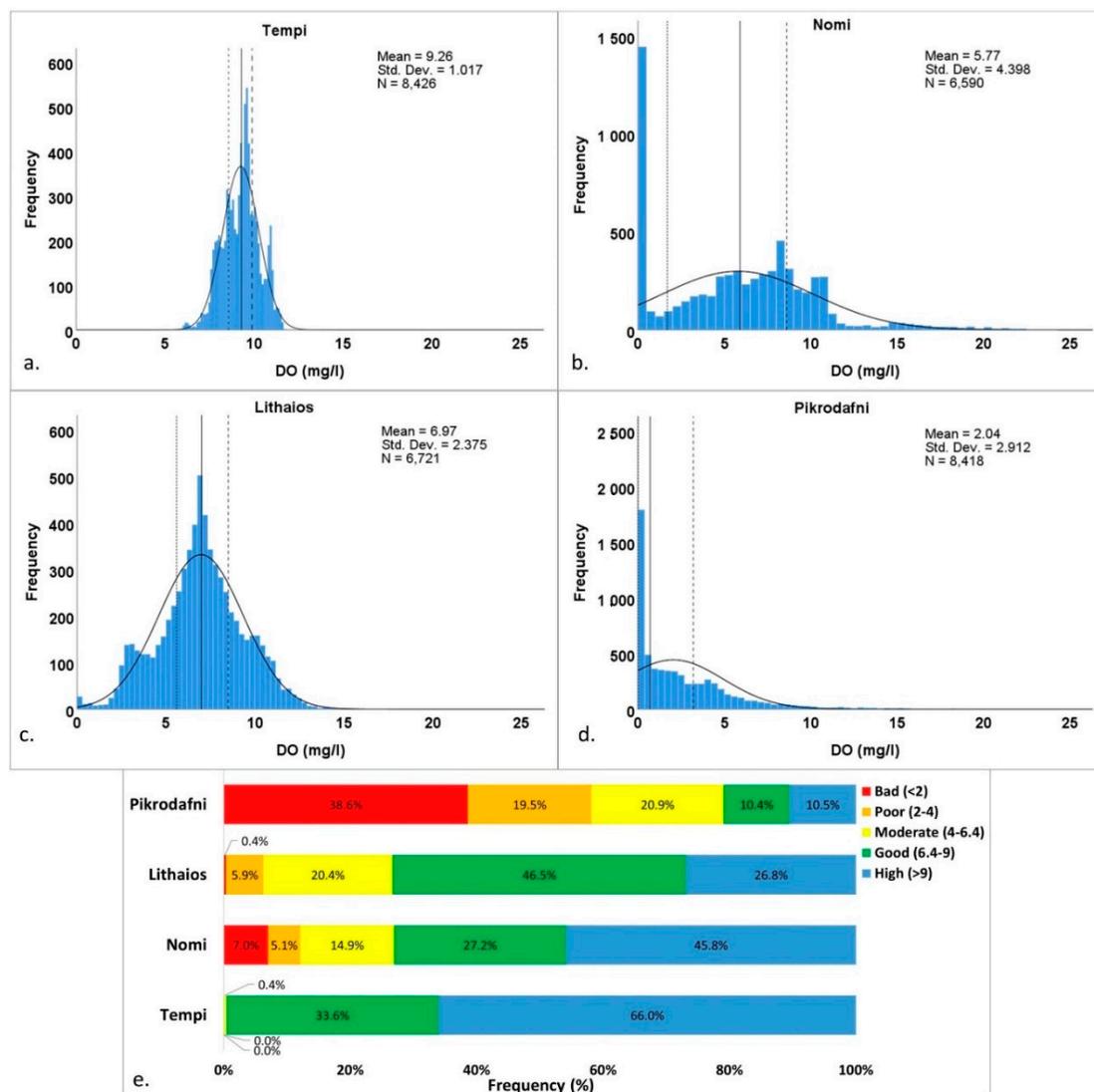


Figure 2. Frequency distribution of DO (mg/L) hourly concentrations for stations (a) Nomi, (b) Tempi, (c) Lithaios, and (d) Pikrodafni (dotted line: 25th percentile, solid line: 50th percentile, dashed line: 75th percentile), and (e) frequency distribution of DO (%) hourly concentrations of monitoring sites per water quality class.

The highest values of electric conductivity in all cases were up to 900 $\mu\text{S}/\text{cm}$, with the exception of Pikrodafni Station, where the maximum value was 1696 $\mu\text{S}/\text{cm}$.

3.2. Time Variations

Based on Figures 3 and 4, water temperature and DO concentrations significantly fluctuated during the day. In the cases of Nomi and Pikrodafni, the range (maximum–minimum) and the interquartile range of hourly water temperature during the day were wider compared to Tempi and Lithaios. Additionally, in Tempi and Lithaios, water temperature showed typical diurnal variation (minimum values around 09:00 and maximum values around 17:00), while at Nomi, and especially at Pikrodafni, temperature daily variations seemed to be controlled by other external factors.

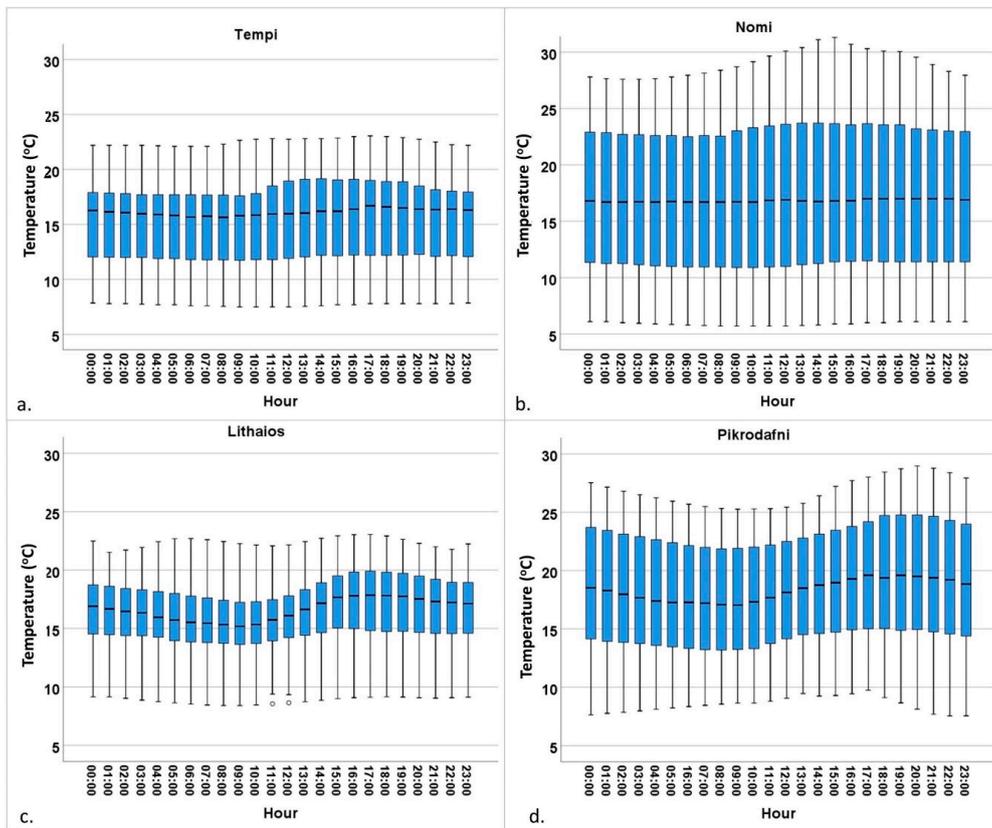


Figure 3. Hourly boxplots of water temperature (°C) for stations (a) Tempi, (b) Nomi, (c) Lithaios, and (d) Pikrodafni.

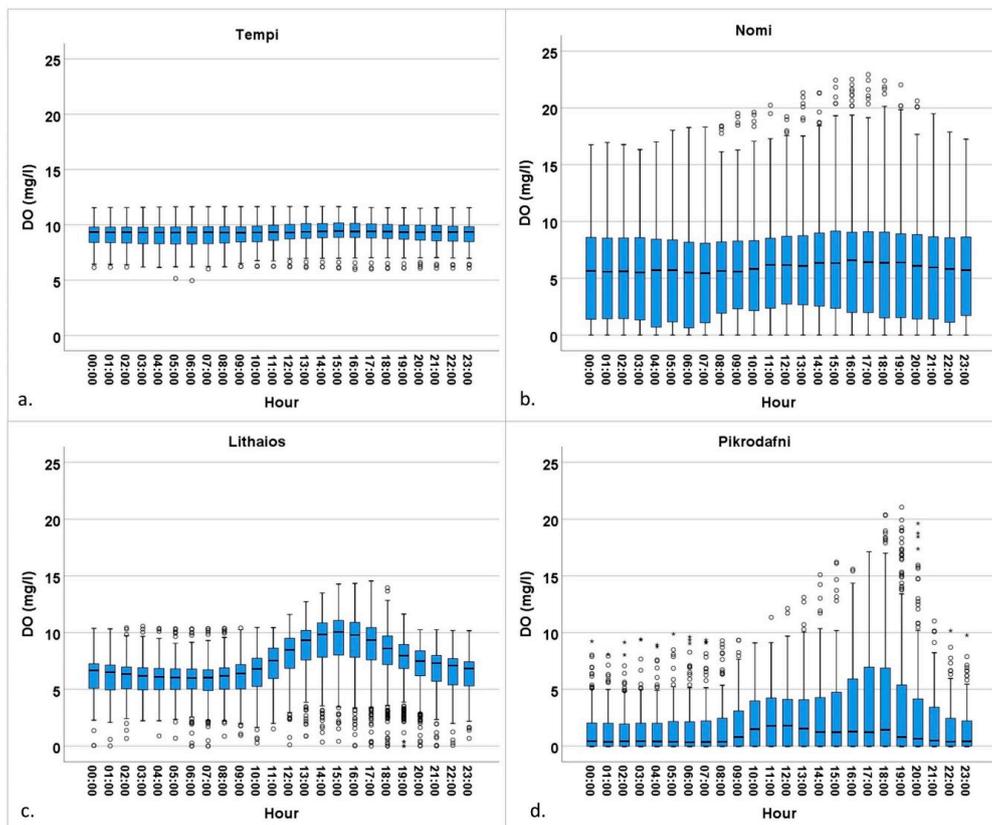


Figure 4. Hourly boxplots of DO (mg/L) for stations (a) Tempi, (b) Nomi, (c) Lithaios, and (d) Pikrodafni.

At Nomi and Pikrodafni Stations, the DO variations were larger and the maximum concentration values recorded were higher than 20 mg/L (Figure 4). In contrast, in Tempi and Lithaios, the maximum DO concentrations were 11.7 mg/L and 14.6 mg/L, respectively. DO concentrations and diurnal fluctuations in the cases of Tempi and Lithaios were milder compared to Nomi and Pikrodafni. In Lithaios and Pikrodafni, the outliers were higher, although in Lithaios, only low outliers were recorded. In Nomi and Pikrodafni, the higher outliers were more pronounced (Figure 5). The diurnal DO concentration fluctuation was typical in Lithaios, gradually increasing during the day, reaching a peak at around 16:00, and then decreasing.

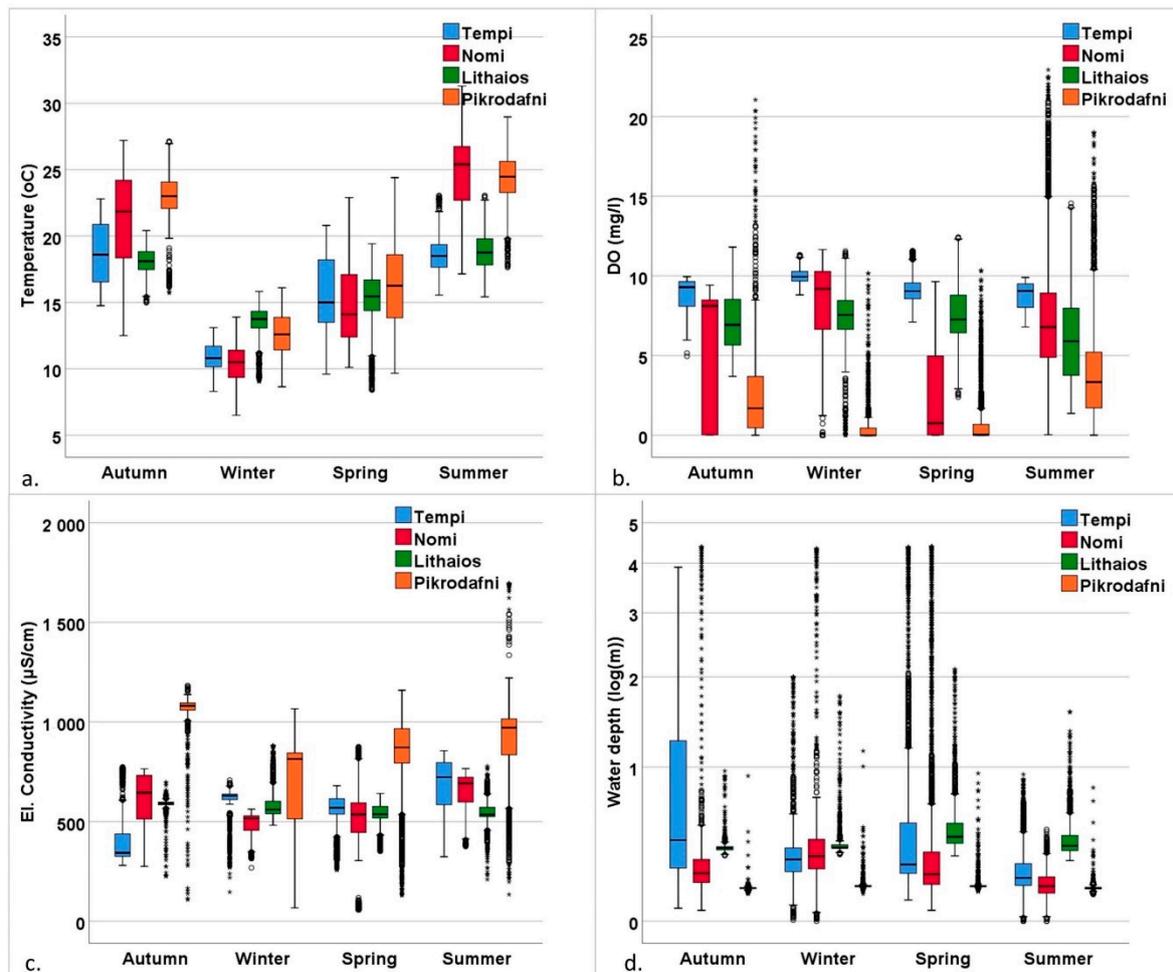


Figure 5. Seasonal boxplots of (a) water temperature (°C), (b) DO (mg/L), (c) EC (µS/cm), and (d) water depth (m).

In Figure 5a, the seasonal variation of water temperature is evident, with the lowest values being reported in winter (December, January, and February) and the highest values in summer (June, July, and August), while in autumn (September, October, November), the water was warmer than in spring (March, April, May). The lowest and highest values were reported at Nomi Station. The seasonal variation of DO was small. However, in Pikrodafni, high outliers were noted during the entire year, while in Lithaios, low outliers were reported in winter (Figure 5b). As shown in Figure 5c,d, the electric conductivity and the water level had no pronounced seasonal variation; however, it can be observed (Figure 5d) that lower water level values occurred at all stations in summer.

Moreover, in Figure 6, the frequency distributions of hourly DO concentrations per month are presented. Based on this figure, at Tempi monitoring station, most of the measurements indicated high to good water quality status, especially in winter (December and January), when the water discharge was also higher. Only in September did there

seem to be some small deterioration of the water quality, which may be due to the first rainfall events after the dry period that drain fertilizer residuals from the basin's soil. At Nomi monitoring station, although in most cases the water quality concerning DO concentrations could be characterized as high or good, the number of measurements classified as moderate or bad was greater than Tempi station. At both sites, a seasonal variation of DO concentration was evident, with higher values occurring in winter.

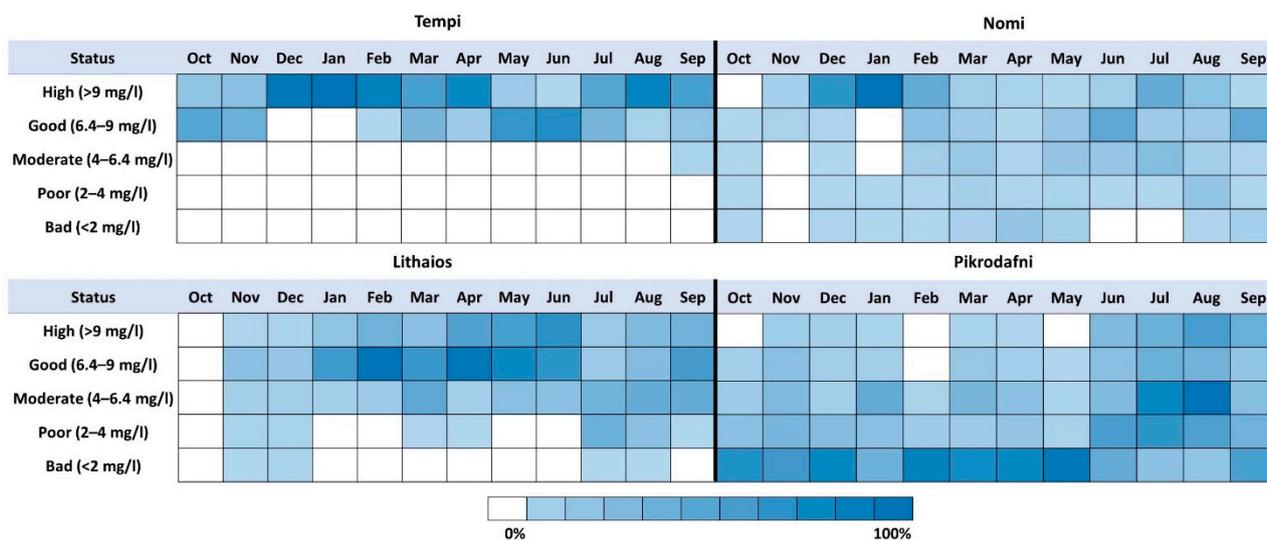


Figure 6. Heatmap of hourly DO concentrations (mg/L) and monthly frequency to the quality status for the hydrological year 2019/2020 (DO classification based on [50]).

Similarly, at Lithaios monitoring station, the majority of the DO measurements were higher than 6.4 mg/L (high to good water quality). Nevertheless, at Pikrodafni station, only 21% of the measurements could be classified in high to good water quality status, whereas the majority of the measurements were classified as bad. The lack of seasonal variation in DO concentration was also evident in the case of the urban sites.

From the distribution of DO values along months and quality classes according to the heatmaps (Figure 6), Tempi was the only site maintaining high and good status, almost always with the vast majority of the measurements being above 9 mg/L (high status). In contrast, the Pikrodafni DO values were distributed throughout the entire spectrum of the natural variations, but with the majority of the measurements less than 6.4 mg/L (moderate to bad status). Nomi and Lithaios Stations were in an intermediate condition, with high variations of DO values, but with most of the measurements being above 6.4 mg/L (good or high).

3.3. Time Series Statistical Analysis

Based on the correlation matrix, the relationship between the basic physicochemical parameters and water level was statistically significant ($p < 0.01$) in all cases (Tables 2 and 3).

Pearson's correlation coefficient R between hourly temperature and DO was negative in the case of Tempi and Lithaios Stations (-0.785 and -0.097 , respectively), although only Tempi could be characterized as high based on the criteria for correlation interpretation proposed by Hinkle et al. [51]. In the cases of Nomi and Pikrodafni, the correlation coefficient between hourly temperature and DO was positive. Electric conductivity and water depth were negatively correlated in all cases. DO concentration did not have a strong correlation with water depth at any site. Finally, the correlation coefficients between DO and EC were negative in the cases of Tempi and Lithaios (-0.244 and -0.351 in Tempi and Lithaios, respectively), while in Nomi and Pikrodafni, the correlations were positive (0.286 and 0.189 , respectively).

The cross-correlogram (CCF) of water depth between Nomi and Tempi Stations was asymmetrical. The highest CCF was achieved after 45 hours, while the value was quite high (0.684), indicating the significant delay in peak discharge appearance between the two sites (Figure 7a).

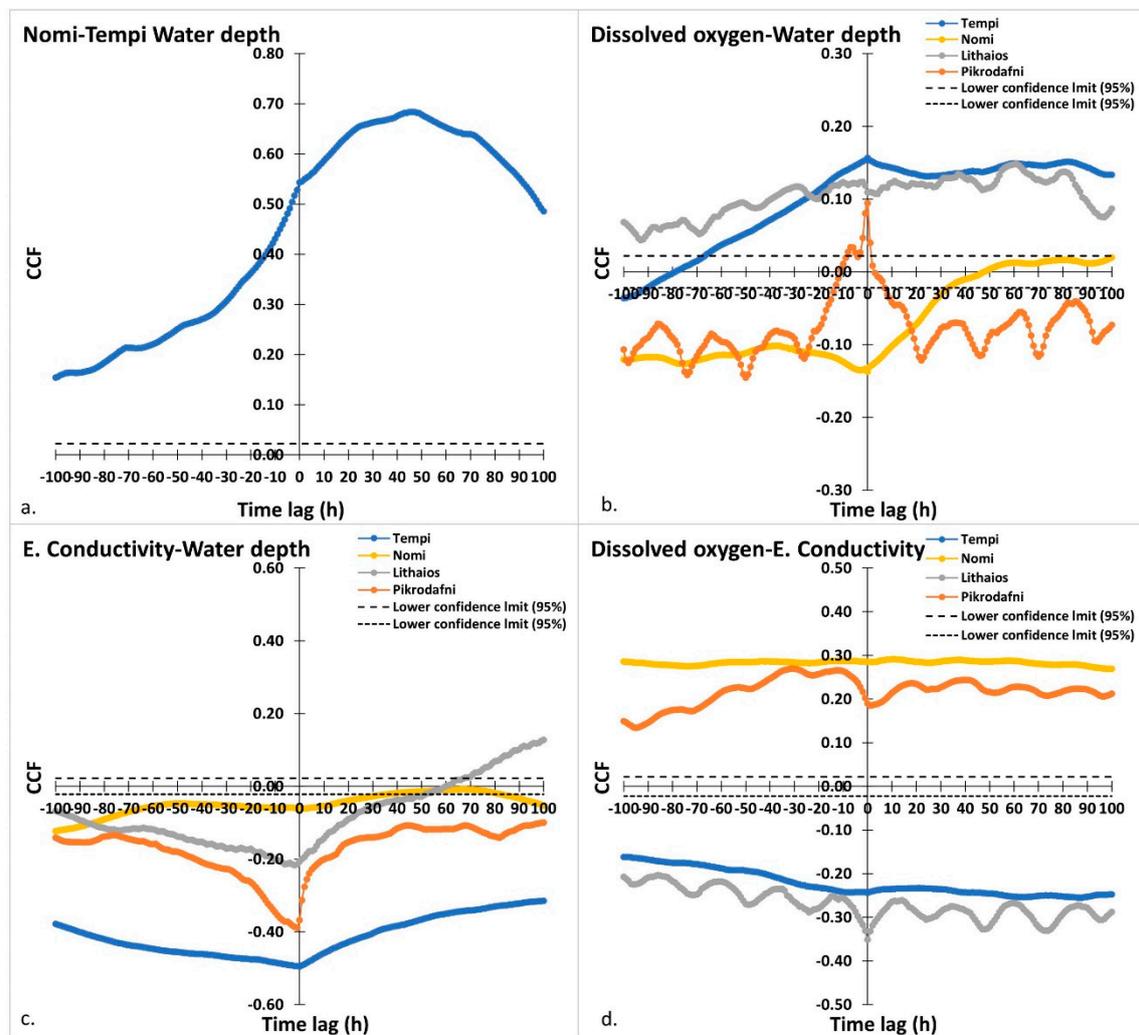


Figure 7. Cross-correlograms (CCFs) of (a) Nomi and Tempi water depth (m), (b) dissolved oxygen (mg/L) and water depth (m), (c) dissolved oxygen (mg/L) and electric conductivity ($\mu\text{S}/\text{cm}$), and (d) water temperature ($^{\circ}\text{C}$) and dissolved oxygen (mg/L).

The cross-correlograms (CCF) between dissolved oxygen and electric conductivity (Figure 7c) and between water temperature and dissolved oxygen (Figure 7d) at Nomi and Pikrodafni Stations demonstrated positive but low values, while Tempi and Lithaios Stations indicated low, negative values. Additionally, no time lag was detected.

The sites at the Pinios River (Tempi and Nomi) demonstrated an evident symmetrical pattern. Nevertheless, at Nomi station, CCF was negative in cross-correlogram between dissolved oxygen and water depth. Similarly, CCF values were positive in the case of Lithaios station and negative in the case of Pikrodafni station in the cross-correlogram between DO and water depth. Finally, the pattern of cross-correlogram in the case of urban monitoring stations was asymmetrical (Figure 7b).

Lithaios and Pikrodafni showed a diurnal variation in the cross-correlograms between DO and water depth (Figure 7b), between DO and electric conductivity (Figure 7c), and between water temperature and DO (Figure 7d), which was stronger at Pikrodafni.

Increase in water depth can be considered to be an indication of an increase in the rivers' discharge, while rapidly moving surface waters tend to have a higher concentration of dissolved oxygen [52]. Similarly, an increase in water temperature leads to lower concentrations of dissolved oxygen [52]. Based on Figure 8a,c, where the RAPS curves of DO and water depth are presented, it was consistent for most of the high peaks at Tempi and Lithaios, as expected. However, the same pattern was not observed in Nomi and Pikrodafni, where in high flows, DO levels either decreased or remained approximately the same (Figure 8b,d). In Tempi and Lithaios Stations, the S_k^{**} values of DO and temperature (Figure 8a,c) were opposite in most cases, while in the case of Nomi and Pikrodafni, this pattern was not obvious (Figure 8b,d). Electrical conductivity showed an opposite fluctuation pattern in relation to water depth at Tempi and Lithaios Stations (Figure 8a,c). Finally, the absence of water depth trend of Pikrodafni Station was evident.

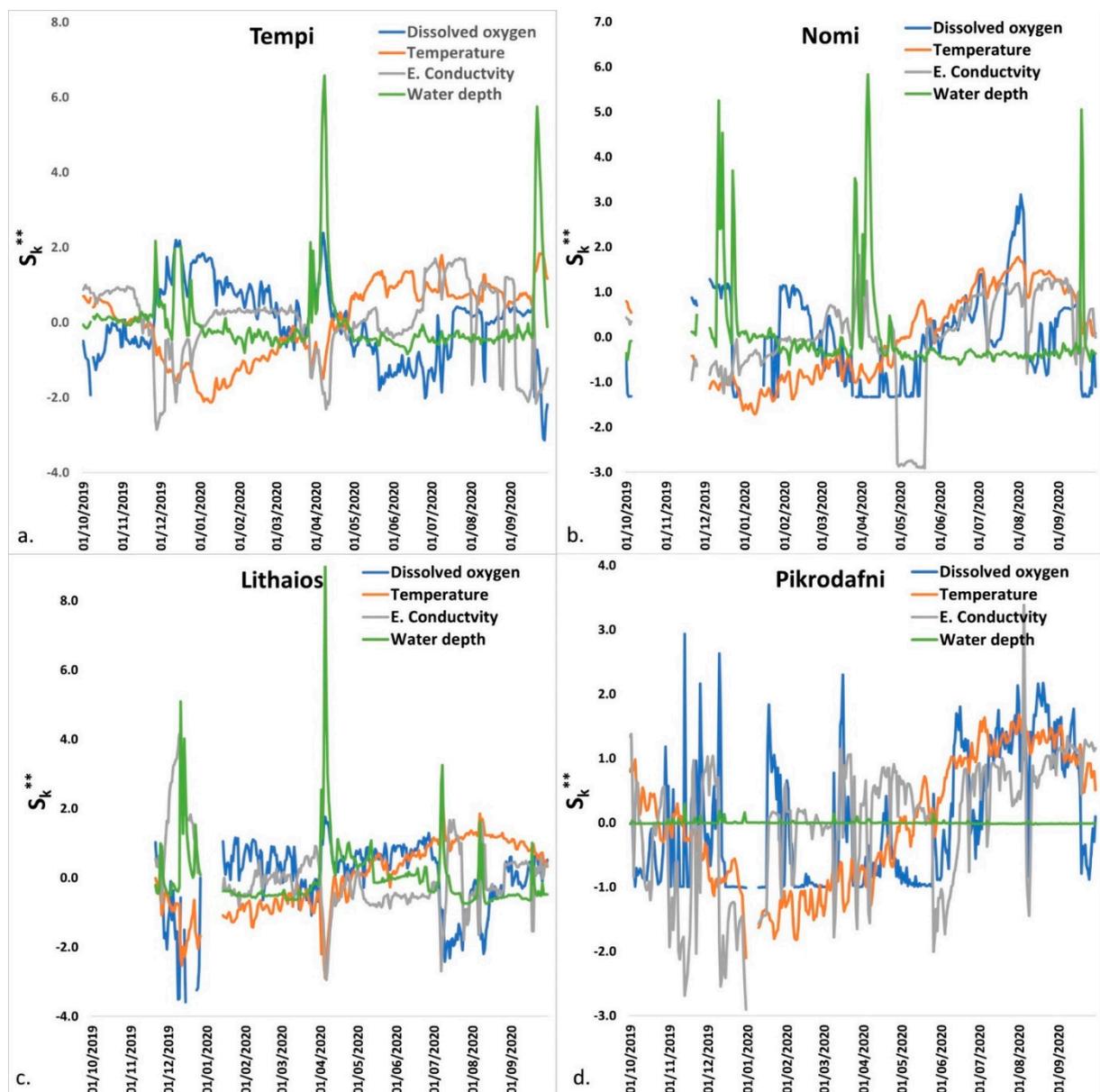


Figure 8. Rescaled adjusted partial sums (RAPS) analysis of daily dissolved oxygen (mg/L), water temperature ($^{\circ}$ C), electric conductivity (μ S/cm) and water depth (m), for monitoring stations (a) Tempi, (b) Nomi, (c) Lithaios, and (d) Pikrodafni.

4. Discussion

Automatic monitoring of surface water bodies can provide the means for high-temporal-resolution water quality and hydrologic observations that would provide the necessary data for understanding the impacts from anthropogenic activities [53]. In the present study, hourly time-series of water level and the main water quality indicators (temperature, electric conductivity, and dissolved oxygen concentrations) obtained from four automatic monitoring stations under different and well-known hydromorphological and pollution pressure conditions were statistically elaborated.

Based on the results, the maximum values and the range of water temperature were higher in the case of polluted stations (Nomi and Pikrodafni stations) compared to relatively unimpacted sites (Tempi and Lithaios stations). Although high values of water temperature can be related to many causes such as air temperature, it is an indication of possible disturbance [52], especially when comparing Tempi, Lithaios, and Nomi stations where the meteorological conditions are similar.

At Tempi station, which is located in an agricultural area with low rate of disturbances, only 0.4% of DO concentrations were classified as below moderate, while at the impacted, agricultural site, Nomi, almost 27% of DO measurements were classified as below moderate. Accordingly, at the urban site, Lithaios, almost 27% of DO measurements were classified as below moderate, and at the highly impacted site, Pikrodafni, 80% of DO measurements were classified as below moderate.

The highest values of electric conductivity in all cases were up to 900 $\mu\text{S}/\text{cm}$, with the exception of Pikrodafni station, where the maximum value was 1696 $\mu\text{S}/\text{cm}$. High electric conductivity values indicate an increase in the dissolved solids concentration, possibly related to pollution; electric conductivity measurements in combination with alkalinity have often been used as a tool in river water quality assessments [54–56]. Values higher than 1000 $\mu\text{S}/\text{cm}$ can be attributed to pollution or large quantities of land run-off [57]; nevertheless, high electric conductivity measurements in urban areas have been reported and may be associated with the wash-off of solutes from hard surfaces [58,59].

Regarding diurnal variations in the cases of impacted sites (Nomi and Pikrodafni), the range (maximum–minimum) and the interquartile range of hourly water temperature during the day was wider compared to unpolluted sites (Tempi and Lithaios). Additionally, in Tempi and Lithaios, water temperature showed the typical diurnal variation (minimum values around 09:00 and maximum values around 17:00), while at Nomi, and especially at Pikrodafni, temperature daily variations seemed to be controlled by other, external factors.

DO concentration variations during the day depended on the characteristics of each station. At stations receiving pollution pressures (Nomi and Pikrodafni), the DO variations were larger. In contrast, at stations without pollution pressures (Tempi and Lithaios), maximum DO concentrations were 11.7 mg/L and 14.6 mg/L, respectively. DO concentrations of diurnal fluctuations in the case of unpolluted sites (Tempi and Lithaios) were milder compared to polluted sites (Nomi and Pikrodafni). At urban sites (Lithaios and Pikrodafni), the outliers were higher, although in Lithaios, only low outliers were recorded. At impacted sites (Nomi and Pikrodafni), the higher outliers were more pronounced. The diurnal DO concentration fluctuation was typical at Lithaios (relatively unpolluted), gradually increasing during the day, reaching the peak at around 16:00, and then decreasing due to the higher oxygen consumption in relation to photosynthesis. Tempi was strongly affected by groundwater springs and therefore the photosynthesis processes, as well as the limited diurnal fluctuations of DO. Moreover, diurnal fluctuations were not evident in the cases of Nomi and Pikrodafni stations, which were impacted by organic pollution and therefore the aforementioned pattern of photosynthetic activity was not evident.

Pearson's correlation coefficient R between hourly temperature and DO was negative in the case of Tempi and Lithaios stations, which is evidence of the antagonistic effect of high temperature to dissolved oxygen solubility. In the case of polluted sites (Nomi and Pikrodafni), the correlation coefficient between hourly temperature and DO was positive, indicating possible external factors affecting the system. Electric conductivity and water

depth were negatively correlated in all cases, as expected, because increased water depths can be associated with recent rainfall events that have relatively low EC values. DO concentration did not have a strong correlation with water depth at any site. Finally, the correlation coefficient between DO and EC was negative in the case of unpolluted monitoring sites (Tempi and Lithaios), while in polluted sites, the correlation was positive (Nomi and Pikrodafni).

The cross-correlogram (CCF) of water depth between Nomi and Tempi stations was asymmetrical. The highest CCF was achieved after 45 hours, while the value was quite high, indicating the significant delay in peak discharge appearance between the two sites.

The cross-correlograms (CCF) between DO and electric conductivity, and between water temperature and DO at Nomi and Pikrodafni stations, demonstrated positive but low values, while Tempi and Lithaios stations indicated low, negative values. Additionally, no time lag was detected. The aforementioned difference in the CCFs supports the aspect that higher pollution pressures are imposed on Nomi and Pikrodafni stations, because the natural relationship between DO and water temperature was reversed in these sites and the expected negative correlation was not met. The cross-correlograms (CCF) between dissolved oxygen and electric conductivity, and between water temperature and dissolved oxygen at Nomi and Pikrodafni stations, demonstrated positive but low values, while Tempi and Lithaios stations indicated low, negative values. Additionally, no time lag was detected. The aforementioned differences in the CCFs support the aspect that higher pollution pressures are imposed on Nomi and Pikrodafni stations, because the natural relationship between DO and water temperature was reversed in these sites and the expected negative correlation was not met. The sites at the Pinios River (Tempi and Nomi) demonstrated an evident symmetrical pattern. Nevertheless, at Nomi Station, CCF was negative in the cross-correlogram between dissolved oxygen and water depth, indicating that an increase in water availability leads to the deterioration of water quality, possibly due to the increase in pollutants during rainfall events that drain agricultural fields.

Lithaios and Pikrodafni, both urban stations, showed diurnal variation in the cross-correlograms between dissolved oxygen and water depth, between dissolved oxygen and electric conductivity, and between water temperature and dissolved oxygen, which was stronger at Pikrodafni, as expected (due to higher pollution pressures).

Finally, based on the RAPS curves, DO and water depth seem to be consistent for most of the high peaks in Tempi and Lithaios. This implies that the significant amount of water entering the system during heavy rainfall was also rich in DO. However, the same pattern was not observed in Nomi and Pikrodafni, where in high flows, DO levels either decreased or remained approximately the same due to the pollution sources existing in the sites' basin. At Tempi and Lithaios stations, the S_k^{**} values of dissolved oxygen and temperature were in most cases opposite, as expected, while in the case of Nomi and Pikrodafni, this pattern was not obvious, which means that there were other factors affecting DO more than temperature at these sites (pollution). Electrical conductivity illustrated an opposite fluctuation pattern in relation to water depth at Tempi and Lithaios stations, which was explained by the low EC values of the rainfall that caused water depth peaks.

5. Conclusions

Socioeconomic development has inevitably led to the qualitative and quantitative degradation of the environment. In particular, riverine ecosystems are subjected to multiple pressures related to hydromorphological alterations and are the recipients of pollution loads mainly associated with agricultural and industrial activities taking place in the watershed [3]. Under these circumstances, integrated river basin management that includes all human activities and the preservation of the environment in a coordinated and sustainable manner [60] requires reliable assessments of surface water quality [61], especially under the challenge of the compliance of the regulation standards set by the EU Water Framework Directive, 2000/60/EC, which aims to maintain and improve the quality of inland and

coastal waterbodies [20]; integrated and economically viable solutions for monitoring and analyzing environmental parameters related to surface water are a necessity.

In this paper, a simple yet effective and low-cost approach based on the statistical analysis of automatic monitoring station data of water level and basic water quality indicators (temperature, electric conductivity, and dissolved oxygen concentrations) has been proposed. The specific framework was based on the analysis of high-frequency measurements at sites with already known hydromorphological conditions and pollution pressures, and provided the means for the interpretation of the current status of the monitoring stations, allowed for the detection of possible changes, and allowed for the definition of thresholds at similar sites. This approach can be used as a textbook example and can be easily reproduced by public agencies or other stakeholders, either locally or regionally, involved in environmental monitoring, public health safety, or civil protection, often lacking in necessary human or financial resources to perform regular environmental monitoring activities. The advent of user-friendly statistical analyses can enable better environmental protection by bridging the gap between data collection, data analysis, and informing decision makers.

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