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Spatiotemporal Variations in Water Physicochemical Status in Pinios River Catchment, at Eastern Mediterranean Region

Stephanos D. V. Giakoumatos [1], Nikolaos T. Skoulikidis [2], Sotirios Karavoltsos [1], Aikaterini Sakellari [1] and Elias Dimitriou [2,*]

[1] Laboratory of Environmental Chemistry, Department of Chemistry, Panepistimiopolis, National and Kapodistrian University of Athens, 157 84 Athens, Greece; sgiak@geol.uoa.gr (S.D.V.G.); skarav@chem.uoa.gr (S.K.); esakel@chem.uoa.gr (A.S.)

[2] Hellenic Centre for Marine Research, Institute of Marine Biological Resources and Inland Waters, 46.7 Km of Athens-Sounio Ave., Anavyssos, 190 13 Attica, Greece; nskoul@hcmr.gr

* Correspondence: elias@hcmr.gr

Abstract: Analyzing water quality variations is essential for the allocation of water to different uses and for applying remedial measures. Thessaly Plain was extremely fertile, and up until the early 20th century, the area was a breadbasket for Greece. The highly important for the national agricultural production, albeit severely degraded Pinios River, has been assessed for its chemical–physicochemical (C-P) status. The research was based on the results of the national monitoring program for the years 2018–2020, considering 218 seasonal samples. A total of 39% of the total samples and 70% of the 30 monitoring stations revealed a lower-than-good C-P status based on Water Framework Directive (2000/60/EC) boundaries. The exceedances are attributed predominately to elevated phosphate, total phosphorous, and nitrate concentrations. Exceptionally, the Pinios River seems to be mainly affected by point sources of organic pollution and secondarily by agricultural return flows and drainage processes, whereas dominant mineralization and nitrification processes control the concentration and type of nitrogen and phosphorus compounds. The coronavirus lockdown seems not to have affected aquatic quality significantly, whereas the improvement of C-P status at the river outflow via dilution by local mountain springs is threatened by an ongoing dry spell affecting the country. Within the upcoming river basin management plans, prompt remediation measures in the Pinios basin should target point sources of pollution and control agrochemicals, particularly focusing on adaptation strategies for extreme weather events.

Keywords: abiotic indices; physicochemical status; river waterbody quality; Pinios River; national monitoring program; eastern Mediterranean

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1. Introduction

Clean and safe water for consumption is a fundamental human right and is essential for the protection of public health and the environment. Thus, surface and groundwater quality management is an issue of high priority in the EU. The first quality targets were set with the implementation of the surface water directive in 1975 and the first drinking water directive in 1980 [1,2]. Later on, Europe's 96/61/EC Integrated Pollution Prevention and Control Directive was set out to address large industrial pollution through new production, operational management, and waste handling approaches, which was a turning point in many aspects [3]. A new water directive (98/83/EC) was introduced a few years later on water quality intended for human consumption [4,5]. According to the aforementioned directive, member states were obliged to take all necessary measures to ensure that water quality intended for human consumption was well monitored and all requirements (including quality standards, organoleptic, and microbiological quality) of the directive were met, as well as drinking-water treatment effectiveness. The Water Framework Directive (WFD) followed in 2000 and introduced new approaches for aquatic ecosystems' health, i.e., 'Good Ecological Status' (abbr. GES) and 'Good Chemical Status.' GES encompasses biological community evaluation and certain hydrological, morphological, and chemical characteristics, surveillance, and operational monitoring [6].

Through the WFD, the EU seeks to improve the effectiveness of existing legislation to address emerging water quality challenges by applying measures to reduce pollution and other pressures on the waterbodies through the introduction of biological assessment methods and the implementation of river basin management plans [7–12].

Climate change [13] incurs extreme phenomena, i.e., prolonged rainfalls, droughts that provoke wildfires, soil erosion, etc., whereas anthropogenic pressure by means of industrial use, intense irrigation, human consumption, and recreational activities exert stress on freshwater resources [14,15]. Thus, surface water bodies of GES are becoming scarce and problematic for consumption, changing surface and groundwater uses and affecting the local economy [15–17].

The Thessaly region, covered with extensive cultivated plots (51% agricultural areas [18–20] and breeding farms), is the most productive plain in Greece, contributing significantly to the national economy. However, overexploitation of water resources and extended agrochemical application [21], in combination with inadequately treated municipal wastewater discharges, exert immense pressures on surface and ground waters [12–18,21,22], while topsoil suffers from erosion and advanced salinization [23,24]. According to Schürings et al. (2024) [22], who applied an Agricultural Pressure Index (API), considering water abstraction, pesticide presence, nitrogen diffusion as fertilizer, and significant hydromorphological interventions, the Pinios catchment was classified among the most degraded in Europe.

The Pinios River basin, which is the main basin of the Thessaly region, annually receives hundreds of thousand tons of fertilizers and thousand tons of pesticides and receives high organic wastewater loads from partly untreated municipal and agro-industrial effluents [25,26]. The latter caused a worsening of ammonium quality during the last decade, despite a general improvement in its C-P status [12]. Shallow groundwaters illustrate dramatic nitrate levels, making them unsuitable for human consumption [27], despite the fact that the basin has been designated a nitrate-vulnerable zone.

Knowledge of river quality variations and exceeding quality limits is essential for the allocation of water to different uses and for applying remedial measures. The scope of the present paper is to detect and study the spatiotemporal variations of the C-P status of the Pinios River catchment and describe the main drivers of these variations in order to implement suitable water resource management tools to support local economies by protecting the environmental status of the river basin.

2. Materials and Methods

2.1. Study Area

The Thessaly region (Figure 1) encompasses two major river basins, namely the Pinios River Basin (code EL0816) and the Almyros—Pilio River Basin (code EL0817) [18]. Overall, seventy-two (72) surface water bodies were identified within the Thessaly River basin district with varying river typologies [28,29]. The Pinios River basin is covered mainly by crops (51%), forests (34%) of various types, and pastures (12%), while urban use (Figure S1, Supplementary Materials) corresponds to 2% of the total area [19]. Eighteen (18) overall municipal Wastewater Treatment Plants (WWTPs) are being operated to service numerous local agglomerations, some of which are significantly dense and vivid in terms of population and industrial activity (see Figure 1). Detailed information on treatment installations is presented in Table S1 (SM) [30]. Officially, only one (1) WWTP located in Karditsa was designated with operational problems and performed nonconformity against EEC 91/271 Directive prerequisites [31] for the period of our interest (2020). WWTPs in the region support urban wastewater secondary treatment with sufficient removal of organic load, nutrients, and Suspended Solids (SSs). In Thessaly are located six designated Industrial Areas (IAs), three of which are in the vicinity of the city of Volos [32]. Volos IAs do not affect the Pinios River water bodies. The other two of our interests are established in Karditsa and Larissa, respectively, supporting various industrial activities mainly of agricultural orientation.

The total annual percentile water consumption is apportioned as follows: irrigation (91%), urban supply (~7%), industrial consumption (1%), and breeding farms (1%). Approximately 84% of the total annual water demand is attributed to abstractions from groundwater bodies by means of boreholes' pumping exploitation to meet mainly irrigation water demand. This turned the natural water balance of the basin to strongly negative [33]. 'Plastira' Reservoir, transferring water from the Acheloos River Basin, covers supplementary irrigation and human consumption needs of the Karditsa municipality administrative area [18].

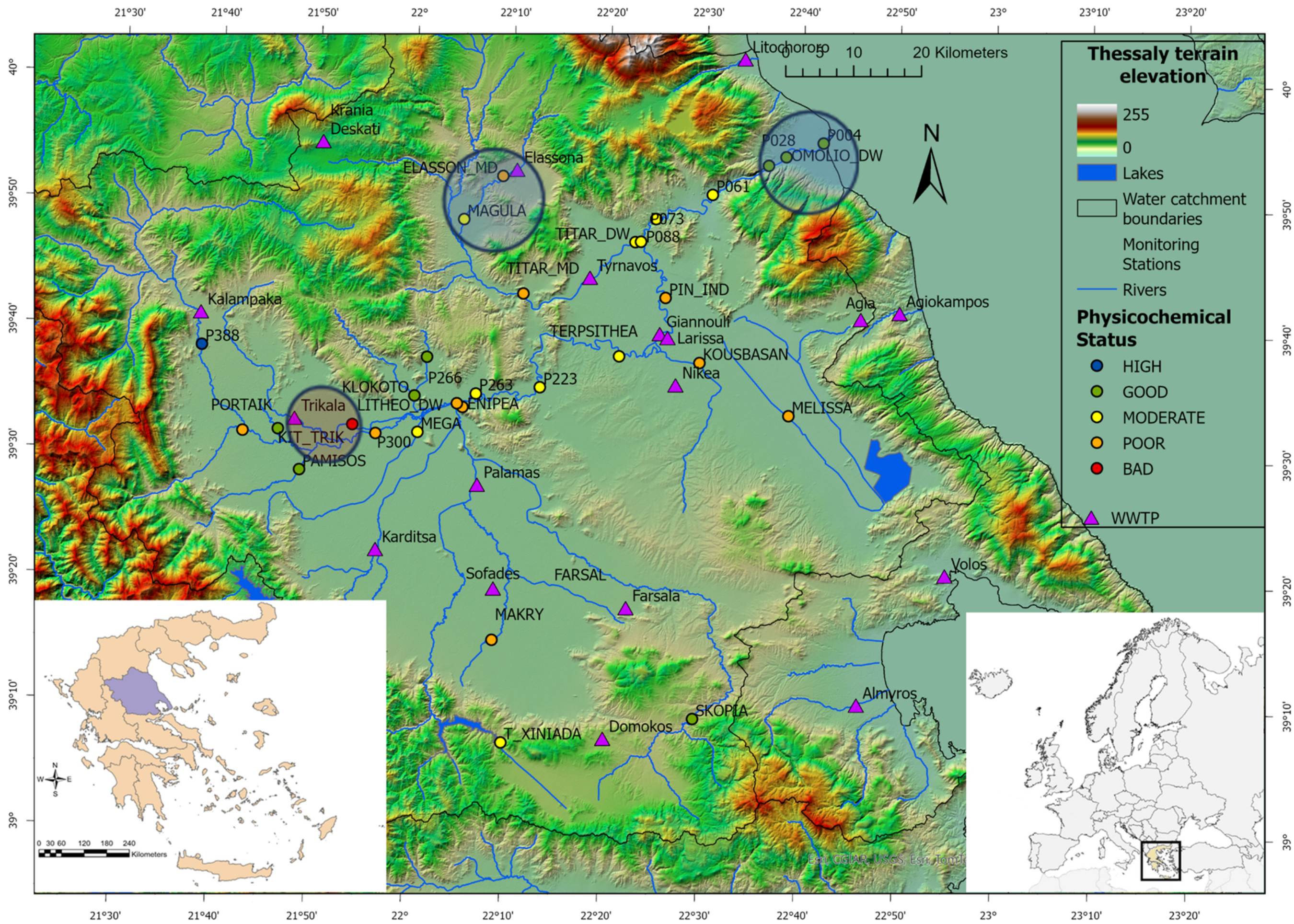

Figure 1. Terrain elevation of Pinios River catchment and physicochemical status of quality monitoring stations (5-quality classes of various colors) [30,34].Wastewater treatment plants (WWTPs) are indicated with purple color triangles (see also Table S1, Supplementary Materials), while sampling stations are depicted by their capitalized site names and their C-P status (see also Table S2, Supplementary Materials).The three light blue circles indicate areas of interest that are further discussed in Section 3.2.

Member States share particular surface water body types and collected data, following the conclusion of Geographical Intercalibration Groups (GIGs). The Pinios basin, covering 11,012 km^2, is classified as very large (>10,000 km^2). It has a mean annual discharge of 1.97 km^3/year, whereas the recent annual fluxes of Dissolved Inorganic Nitrogen (DIN) and P-PO$_4$ were estimated to be 1.51 and 0.17 kt, respectively [35]. Regarding 'very large' rivers, Greece is intercalibrated for river type R-L2. The characteristics of the different river types are presented in Table S3, Supplementary Materials.

2.2. Sampling and Analysis

In this study, water quality data from Thessaly Rivers from the period 2018–2020 were considered and collected under the national monitoring program for the assessment of the ecological status of Greek rivers, led by the Institute of Marine Biological Resources and Inland Waters of the Hellenic Centre for Marine Research (HCMR), according to the WFD provisions [36]. Seasonal data regarding nutrients (nitrates, nitrites, ammonium, and phosphates), turbidity, dissolved oxygen, water temperature, electric conductivity, chloride, and pH have been deployed from the WFD database of the HCMR, covering 30 stations within the Thessaly region (Table 1). In total, two hundred and eighteen (218) samples were collected, and the dataset is available here: https://doi.org/10.5281/zenodo.13646661.

Table 1. Sampling stations with their unique (ID) coding with a brief description, Pinios River tributaries classification according to Med. rivers intercalibration results and coordinates (WGS 84). River types are presented in Table S3, Supplementary Materials [36].

A/A	Description	ID Code	Internal River Type	WGS 84	
1	ELASSON_MD	EL0816R000202310N200	RM-2	39.87154	22.14997
2	ENIPEA	EL0816R000206023N050	RM-3	39.56352	22.08793
3	KIT_TRIK	EL0816R000214050N050	RM-4	39.53001	21.77237
4	KLOKOTO	EL0816R000210143N050	RM-2	39.57768	22.00542
5	KOUSBASAN	EL0816R000204018H050	RM-5	39.62813	22.49353
6	LITHEO_DW	EL0816R000210042N050	RM-4	39.53783	21.89975
7	MAGULA	EL0816R000202310N250	RM-5	39.81298	22.08429
8	MAKRY	EL0816R000206228N050	RM-1	39.25533	22.14608
9	MEGA	EL0816R000208040N050	RM-2	39.52941	22.01166
10	MELISSA	EL0816R000000064A050	RM-2	39.55914	22.64729
11	NEOXOR	EL0816R000210144N050	RM-5	39.62949	22.02573
12	OMOLIO_DW	EL0816R000201002N250	VERY-LARGE	39.90307	22.63763
13	P004	EL0816R000201002N300	VERY-LARGE	39.92188	22.70157
14	P028	EL0816R000201002N200	VERY-LARGE	39.89149	22.60745
15	P061	EL0816R000200004N050	VERY-LARGE	39.85138	22.51186
16	P073	EL0816R000200005N050	VERY-LARGE	39.80690	22.39901
17	P088	EL0816R000200015N100	RM-3	39.78782	22.38942
18	P223	EL0816R000200022N250	RM-4	39.59194	22.22036
19	P263	EL0816R000200022N300	RM-4	39.58204	22.11037
20	P266	EL0816R000200039N150	RM-4	39.56857	22.07846
21	P300	EL0816R000200039N100	RM-4	39.52668	21.94005
22	P388	EL0816R000200053N100	RM-4	39.63924	21.63874
23	PAMISOS	EL0816R000212048N050	RM-4	39.47621	21.81038
24	PIN_IND	EL0816R000200015N150	RM-3	39.71346	22.43364
25	PORTAIK	EL0816R000216051N150	RM-4	39.52651	21.71220
26	SKOPIA	EL0816R000206038N100	RM-4	39.15482	22.49110
27	TERPSITHEA	EL0816R000200020N050	RM-3	39.63472	22.35500
28	TITAR_DW	EL0816R000202006N050	RM-3	39.78685	22.38000
29	TITAR_MD	EL0816R000202007N100	RM-5	39.71589	22.18866
30	T_XINIADA	EL0816R000206235A050	RM-1	39.11937	22.16460

All data derived by means of field sampling and laboratory analyses (for sampling and laboratory analysis procedures, please refer to [36]) underwent data processing by combined data analysis techniques. Each sampling station was assigned a unique ID code and a brief description. Furthermore, the Pinios tributaries' network was classified in accordance with the Med-river bodies intercalibration exercise preceded to define type-specific reference conditions [28,29], as given below in Table 1.

2.3. Data Analysis

Evaluation of the C-P status was accomplished by employing methodologies developed according to the implementation of WFD [6] and the latest adopted Pinios River Basin Management Plans (RBMPs). For that purpose, nutrients and DO data were collected from all involved monitoring stations of the operational water monitoring network. Each individual parameter value received a score compared to defined thresholds [34], and the overall average score provided the final status C-P classification (Table S4, Supplementary Materials) [37]. Dissolved Inorganic Nitrogen (DIN) comprises the sum of ($N\text{-}NO_3$), ($N\text{-}NH_4$), and ($N\text{-}NO_2$). Total Nitrogen (TN), which is the sum of DIN and nitrogen bound to Organic Matter (ON), determined the trophic state [38,39] (Table S2, Supplementary Materials).

Significant information is received from cross-correlation matrices. Correlations were tested pairwise between measured parameters, making use of the mean concentration of all involved monitoring stations (Table S5, Supplementary Materials). In general, weak correlations prevailed as a result of overlapping, opposing processes [40] running in the Pinios River basin (e.g., photosynthesis versus respiration, nitrification versus denitrification) [41]. Thus, for the interpretation of the results, even weak correlations were used that suggest the prevailing processes taking place.

Box plots were used in order to extract information contained in periodical samplings conducted on a regular monitoring basis. They are widely used in descriptive statistics for graphically demonstrating the locality, spread, and skewness of numerical data through their quartiles.

Intense rainfalls in the winter of 2018 seriously affected the investigated parameters by means of extended runoffs and subsequent flashing and/or dilution in river bodies. Therefore, rain precipitation and temperature in four meteorological stations (Table S6, Supplementary Materials) were recorded and interrelated to the obtained results to quantify the degree of influence according to the published data of the National Observatory of Athens (NOA) (Figure S2, Supplementary Materials) [42].

3. Results

3.1. Temporal Variations in Physicochemical Status

3.1.1. Inter Annual Variations

In terms of rainfall fluctuations, except for the beginning of 2018, during 2019–2020, no remarkable differences were observed in most active meteorological stations (Table S6, Supplementary Materials) of NOA in the region of interest [42]. Intense rainfall recorded in December 2017 and winter 2018 (Figure 2a) is reflected in temporarily increased turbidity measurements via an increase in turbidity physical index (NTU) (Figure 3b). Persisting precipitation significantly affects river water turbidity values since soil weathering and erosion phenomena occur, which enhances particulate matter transportation, fertilizer, and organic matter washing off from agribusiness facilities/activities.

Throughout the sampling period (2018–2020), median and average TN values were steadily above the 'mesotrophic state' boundary, while the vast majority of measurements were above the oligotrophic threshold, belonging to the mesotrophic and eutrophic trophic statuses (Figure 3b; Table S2, Supplementary Materials). The year 2019 was the worst period in terms of TN concentrations since both average and median concentration values were higher than those of 2018 and 2020, exceeding the mesotrophic/eutrophic boundary (i.e., 1.5 mg L^{-1}), though a greater diaspora of values was demonstrated.

The ammonium median value appeared to lie steadily within the 'Good Status' band in all years studied (Figure 3a), with median and average values lying closely at a small distance to the good/moderate quality boundary. The years 2019 and 2020 display great similarities depicted in the fluctuation range regarding the ammonium concentration footprint. Measurements recorded in 2018 are somewhat within a narrow range. Individual monitoring stations (Table 1) described as 'KUSBASAN', 'SKOPIA', 'KIT_TRIK', and, to a smaller extent, 'LITHEO_DW' demonstrate high ammonium values all year round.

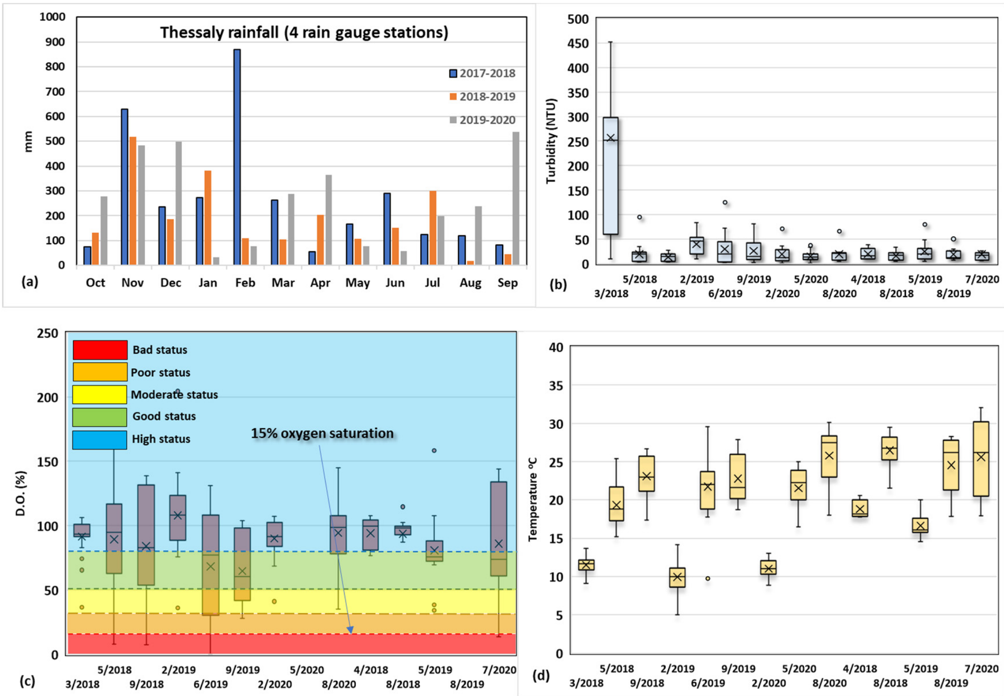

Figure 2. (**a**) Variation in seasonal rainfall in 2018–2020, based on data collected from four rain gauge stations (Table S6, Supplementary Materials) [42]. (**b**) Turbidity measurements at all monitoring stations in the Pinios basin (2018–2020) at predefined sampling periods. (**c**) Dissolved Oxygen (DO) saturation in river waterbody and (**d**) temperature, measured at all monitoring stations in the Pinios basin (2018–2020) at predefined sampling periods [36,42].

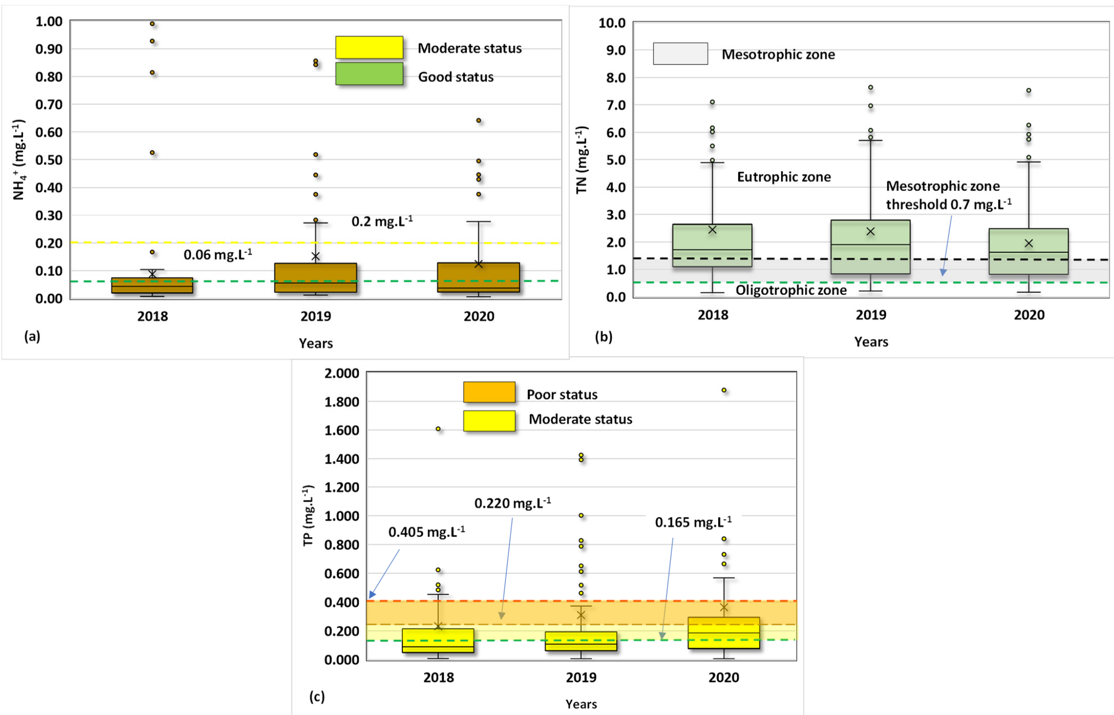

Figure 3. (**a**) Variation in ammonium measurements in the years 2018–2020. Green and yellow dashed lines denote 'Moderate' and 'Good' status thresholds, respectively [34]. (**b**) Variation in TN measurements in the years 2018–2020. The gray-colored band denotes the mesotrophic state area [38,39]. (**c**) TP measurements in the years 2018–2020. Green, orange, and red dashed lines denote 'Good', 'Poor', and 'Bad' status thresholds, respectively [34].

The boxplots for the Total Phosphorus (TP) indicate that almost 50% of the measurements were classified within the 'Poor' and 'Moderate' TP status zones in the years 2018 to 2020. In 2019, only nine 'outliers' exceeded the upper 'Bad Status' value threshold (Figure 3c). The TP median values in the years 2018 and 2019 were below the Good/Moderate boundary, and the average value lay within the 'Poor Status' band (see Table S2, Supplementary Materials). In 2020, the highest TP concentration values were reported, with more than 40% being classified as poor or bad quality.

3.1.2. Intra Annual Variations

Field measurements demonstrate a remarkable fluctuation of Dissolved Oxygen (DO) values all year round. In the vast majority of the results, DO average and median values steadily exceeded 50% of the oxygen saturation zone (Figure 2c), denoting the prevalence of 'good' and 'high' oxygen status according to Table S2, Supplementary Materials. In addition, only 5% of DO measurements revealed hypoxic conditions, i.e., concentrations below 3 $mg{\cdot}L^{-1}$. Finally, the dissolved oxygen concentration was inversely correlated to water temperature, as verified by the cross-correlation (Figure 2d; Table S5, Supplementary Materials).

Apart from a few scattered measurements, the largest proportion of samples in terms of orthophosphate were plotted within the high/good quality zones, at least till the end of the summer of 2019 (Figure 4a).

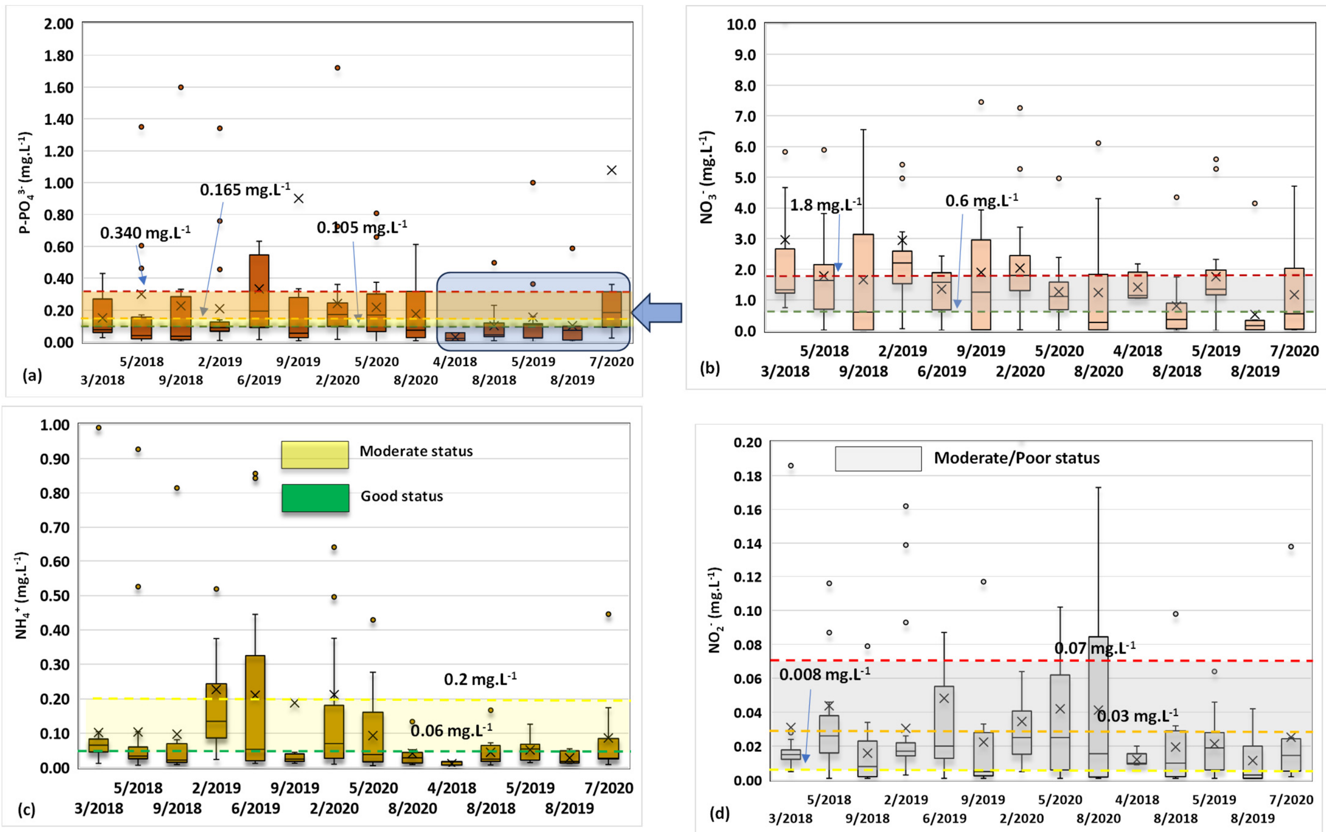

Figure 4. (**a**) Orthophosphate concentration fluctuation (2018–2020). The bluish frame corresponds to the COVID pandemic lockdown period in Greece [34]. (**b**) River waterbodies nitrate concentration was measured at all monitoring stations in the Pinios basin (2018–2020) at predefined sampling periods. The green dashed line defines the boundary value between good/moderate status [34]. (**c**) Ammonium and (**d**) nitrite concentrations were measured at all monitoring stations in the Pinios basin (2018–2020) at predefined sampling periods. Quality classes, according to [34].

Only in August 2018 and 2019, river water bodies sustain a "Good Nitrate Status" (Figure 4b) (see Table S2, Supplementary Materials). On the contrary, in September 2018 and 2019, a clear deterioration of nitrate quality was apparent, with the average lying almost at the poor/bad status boundary. Ammonium (Figure 4c; Table S2, Supplementary Materials), and especially TP and chloride anions (Cl^-), present a positive correlation with BOD (Table S5, Supplementary Materials). The mean value of the fraction (organic phosphorus/TP) is estimated to be 0.31. Apart from August 2020, river waterbodies' nitrite quality lies below the 'Bad status' zone (Figure 4d; Table S2, Supplementary Materials). The majority of the measurements lie within the 'moderate/poor status' zone.

3.2. Spatial Variations of Chemical–Physicochemical Status

Elassonitis, a tributary of the Pinios River, downstream 'Elassona' site WWTP at the 'ELASSON_MD' monitoring station (Figure 1) interest area depicted in bluish circle, and (Table S1, Supplementary Materials), demonstrates high TP, moderate ammonium values, elevated chloride concentration (4 out of 8 measurements exceed 70 $mg \cdot L^{-1}$, the upper accepted level for unconcerned plant growth after irrigation [43,44]), and a 'poor' C-P classification. A further downstream station named 'MAGULA' (Figure 1), an interesting area depicted in a reddish circle, receives a better 'moderate' C-P classification. Nonetheless, it displays as high as the former station TP concentration. 'LITHEO_DW' demonstrates 'bad' C-P status, even though the upstream 'Trikala' WWTP (Table S1, Supplementary Materials) seems to operate smoothly, i.e., within EEC 91/271 guidelines [30,31].

The last three sequenced monitoring stations located just before the deltaic zone 'P004', 'OMOLO_DW', and 'P028' (Figure 1, interest area depicted in a bluish, on the right side located circle), demonstrate a 'Good' C-P classification, albeit a few km upstream river quality is barely 'moderate.'

RM-5 river types display the highest ammonium values, followed by RM-4 and RM-3 (Figure 5c). LITHEO_DW station (i.e., RM-4 type) demonstrates the maximum ammonium values. In 2020, the WWTP of Karditsa was recorded by the competent Greek ministry (Hell. Min. Env. Ener., 2024) as non-compliant with EEC 91/271 regulated limits, as regards (BOD_5, COD). Therefore, there is strong evidence that sampling results from the above-given monitoring station are negatively affected by inadequate urban wastewater treatment.

Regarding TP, 'RM-5' rivers demonstrate significant median values, considerably higher than the other river types (Figure 5a). The second-ranked is the river type 'RM-2'. Moreover, 'RM-5' river sampling values present a great TP diaspora. A high percentage, i.e., more than 75% of 'Very large' rivers' TP sampling values are placed in 'good' and 'High Status' (Figure 5a). Orthophosphates present almost the same pattern (Figure 5b) since they demonstrate the highest contribution to the TP. RM-1 and RM-4 river types demonstrate the highest $N\text{-}NO_3$ measured values (Figure 5d).

RM-3 and, i.e., RL-1 and RL-2 types (see Table S3, Supplementary Materials) are all rich in water and display the best quality as regards the TN parameter, presumably due to the high dilution potential (Figure 6a). RM-1 type, i.e., small streams with a catchment <100 km^2, demonstrate marginally the higher median concentration as regards nitrogen chemically bound to organic matter (ON). RM-2 medium-size streams and RM-3 very large rivers display almost the same median (Figure 6b).

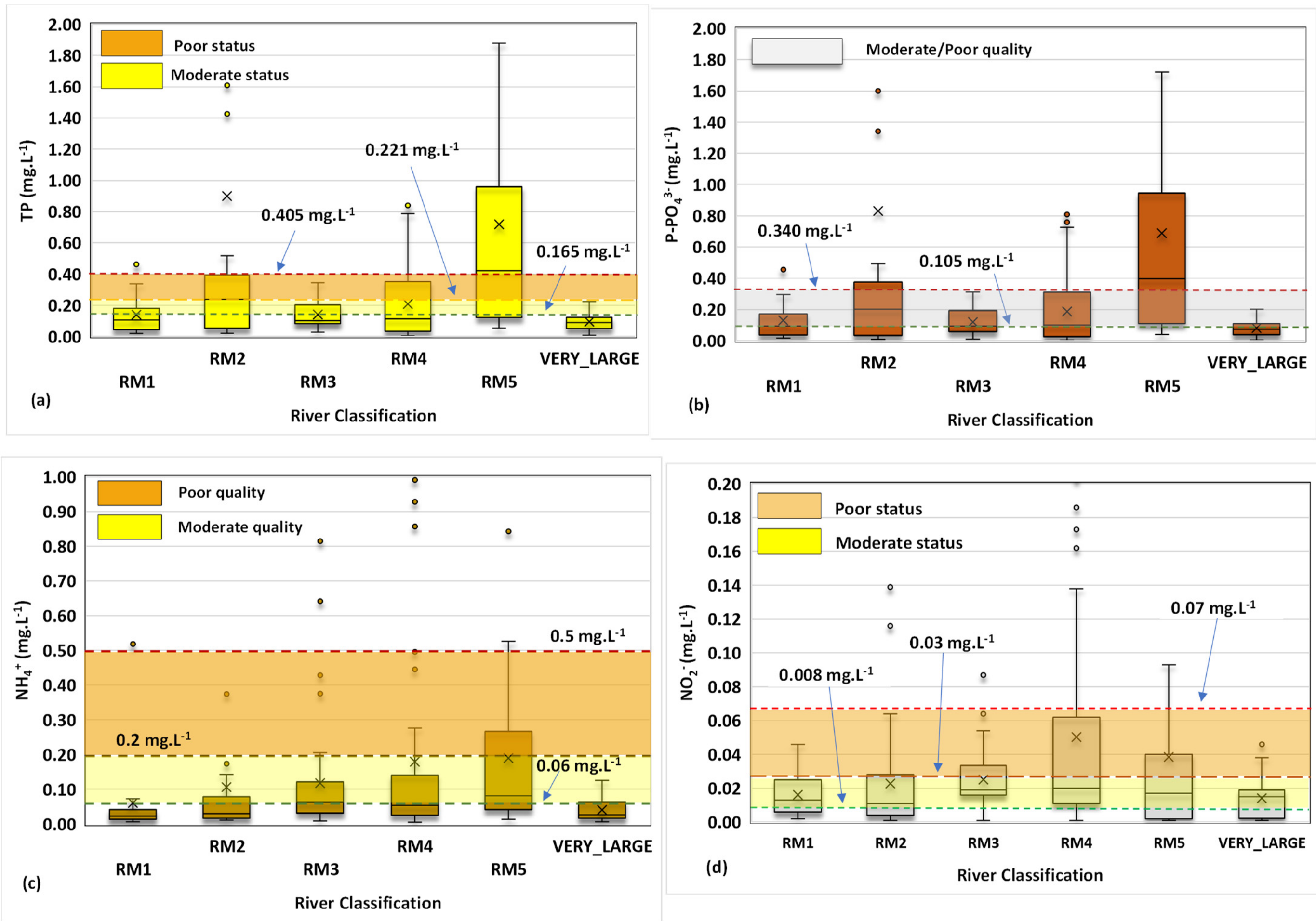

Figure 5. (**a**) River waterbody's total phosphorus concentration [34] was measured at all monitoring stations in the Pinios basin (2018–2020) at predefined sampling periods. (**b**) Overall orthophosphate anions concentration [34]; (**c**) ammonium cations concentration; (**d**) nitrate concentration measured within the 2018–2020 period for various classified Med-river types. Quality classes [34].

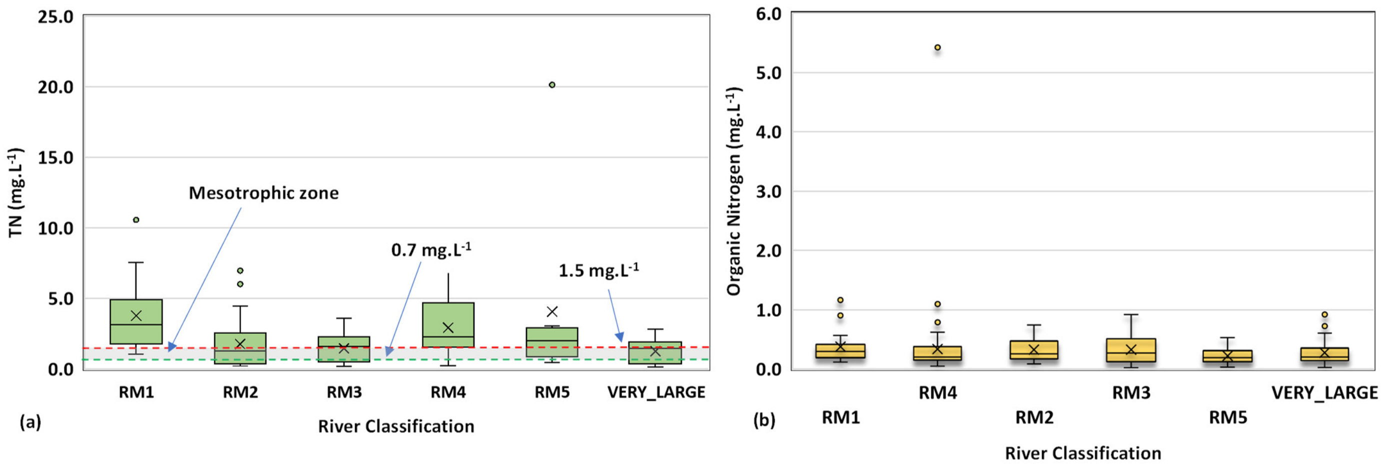

Figure 6. (**a**) Overall total nitrogen concentration. Trophic status classification after [38,39]. (**b**) Organic nitrogen in different river types.

3.3. Management Issues

In Figure 7, an overall assessment of the C-P status in the Pinios River catchment is presented based on nutrients (i.e., N-NO_2, N-NO_3, N-NH_4, P-PO_4, TP, TN) and Dissolved

Oxygen (DO). One hundred and three (103) samples from thirty (30) monitoring stations were classified as 'Good Status', fifty-seven (57) as 'Moderate', and twenty-nine (29) as 'High Status' samples. A total of 62% of the measurements achieve a C-P satisfactory status. The results entail extensive rehab actions to be taken for the C-P improvement.

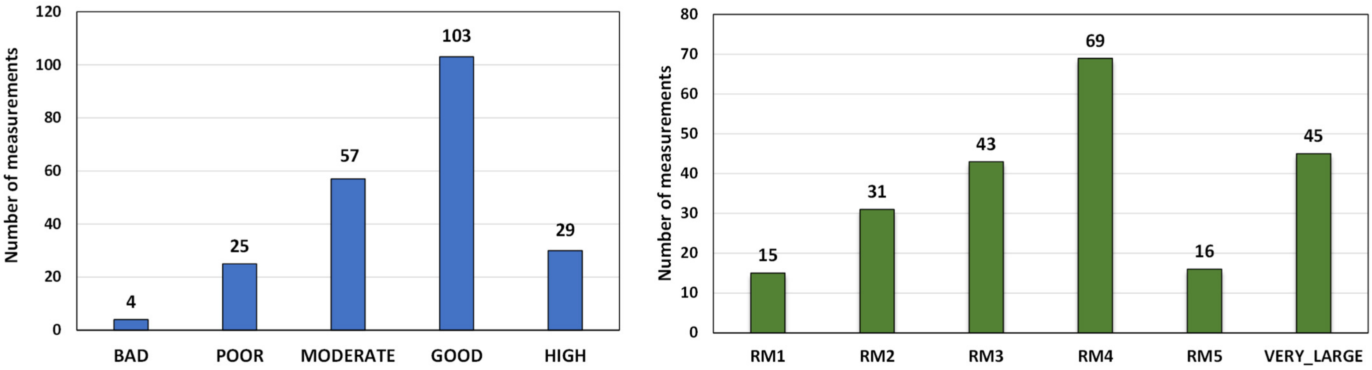

Figure 7. The physicochemical status of the operated monitoring stations at Pinios river catchment in the Thessaly and Sterea Ellada in central Greece.

Moreover, 86 out of 218 measurements, i.e., 40%, revealed a lower than good C-P status. From this total, only half of DO presented a lower-than-good quality, along with 65% of ammonium, 72% of nitrite, and 89% of TP measurements. Regarding nitrate and phosphate, 83% and 95% of the measurements presented a lower-than-good quality. Monitoring stations considered to be heavily burdened by nutrients are the sites depicted in Table 2.

Table 2. Monitoring stations with below-seasonal good C-P status (moderate/poor/bad) in the period 2018–2020 (overall 86 non-'GES' compliances out of 218 samples collected).

Station Description	C-P Status Moderate	C-P Status Poor	C-P Status Bad	TP Limit Exceedance	$P\text{-}PO_4$ Limit Exceedance	$N\text{-}NH_4$ Limit Exceedance	$N\text{-}NO_3$ Limit Exceedance	DO Limit Exceedance
ELASSON_MD	4	4	0	8	8	6	2	6
ENIPEA	2	1	0	2	2	3	2	3
KOUSBASAN	2	2	0	3	3	3	2	1
LITHEO_DW	0	5	4	9	9	7	9	9
MAGULA	5	0	0	5	5	3	1	3
MAKRY	4	1	0	4	4	3	5	3
MEGA	1	0	0	0	1	1	1	1
MELISSA	6	1	0	7	7	1	7	6
P061	3	0	0	2	3	2	3	1
P073	2	0	0	2	2	1	2	1
P088	4	0	0	4	4	2	4	2
P223	5	0	0	4	5	3	4	3
P263	4	0	0	3	4	3	4	4
P266	2	2	0	4	4	3	4	3
P300	2	3	0	5	5	3	5	5
PIN_IND	0	3	0	3	3	3	3	2
PORTAIK	1	2	0	2	3	3	3	1
T_XINIADA	1	0	0	1	1	1	1	0
TERPSITHEA	4	0	0	4	4	2	4	2
TITAR_DW	2	0	0	2	1	1	2	2
TITAR_MD	3	1	0	3	4	4	4	0
Sum	**57**	**25**	**4**	**69**	**74**	**52**	**70**	**52**

According to Table 2, quality limit exceedances were detected at 35.8% of the overall monitoring sampling sites. Particularly, 21 out of 30 (Tables 1 and 2) monitoring stations demonstrated C-P status lower than 'good' in 86 seasonal measurements, i.e., a percentage of 70%.

Despite high organic wastewater inputs in the Pinios basin, the average basin ON comprises only 14% of TN. To compare, the average ON percentage in the Evrotas basin, which receives agricultural and organic agro-industrial effluents, equals 37.1 [45], whereas the average ON percentage in the almost undisturbed Krathis river basin reaches 76.5 [46].

4. Discussion

In the Pinios basin, DO values showed that surface waters are mostly under oxidizing conditions, despite the impact of organic wastewater. DO values in Table 2 demonstrate similar levels of good status exceedance as ammonium, i.e., 52, followed by nitrates and orthophosphates with 70 and 74 samples, respectively. The middle course of the river displays the worst performance in terms of C-P quality.

Dissolved oxygen concentration was inversely correlated to water temperature [47], as verified by the cross-correlation matrix (Table S5, Supplementary Materials) and the literature. In addition, DO revealed negative correlations with BOD and TP (Table S5, Supplementary Materials), indicating the occurrence of organic matter decay processes and denoting that oxygen reduction during the dry seasons is attributed to the combined effect of oxygen consumption due to decomposition of organic matter and the increase in temperature. Hence, organic matter decay processes, especially during low flow periods, seem to mask enhanced photosynthesis favored by prolonged daylight, high temperatures, and nutrient availability [40,48,49], deteriorating oxygen concentrations and violating good oxygen quality in half of the samples.

Nitrates are highly involved in cases where C-P status quality falls short of good. The main source of nitrates in Greek rivers (including Pinios) concerns inorganic nitrogen-based fertilizers [50]. Considering that the Pinios basin is covered by over 24% by irrigated cultivations [51] and that vast cropland areas are in proximity to river courses, autumn and winter floods favor flushing of fertilizers (applied to crops mainly in autumn and winter periods) from cultivated topsoil, which in turn gives rise to nitrate concentration. These incidents do not take place quantitatively in the dry period of the year, as the negative correlation between nitrate concentrations and water temperature indicates (Table S5, Supplementary Materials). The relatively low nitrate concentrations observed in non-perennial RM-5-type rivers may be attributed to low flow and restricted flood events that prevent excessive land flushing processes. Finally, it is not to be excluded that nitrate increases during high flow seasons (coinciding with high oxygen concentration) may be additionally caused by enhanced nitrification processes [41]. Most of the samples regard RM-4 type rivers, which indicates that seasonal phenomena are most probably C-P classification controllers.

In Pinios River, orthophosphate is the nutrient element that violates good quality in almost all measurements, lying below good C-P status. Orthophosphate is a major industrial chemical agent, a component of many commercial products, with large temporal applicability, utilized as a fertilizer, and usually reaches river water during arable land flushing [45,46]. In the particular catchment, however, the positive correlation between water temperature and P-PO_4/TP suggests an additional enrichment mechanism: extensive animal-derived bio-fertilizers used as a recycled byproduct from local vivid breeding farm activities (i.e., pigs, cattle, and poultry) applied in warm periods, together with inadequately treated municipal wastewaters and ones derived from seasonal food industries operating in summer, temporally coinciding with a very poor water flow. These activities, in combination with organic matter mineralization processes, seem to override the leaching of phosphate fertilizers from agricultural land during high-flow events. Similarly, WWTP malfunctioning, along with seasonal food industry and livestock activities, gives rise to TP, ammonium, and chloride (since Cl^- is contained in urea), as the positive correlation indicates, between TP, ammonium, and chloride with BOD. The impact of WWTPs is clearly demonstrated at the Elassonitis tributary, which receives a 'poor' C-P classification ('ELASSON_MD' station) due to the effluents of the upstream operating WWTP on the site "Elassona" (Table S1, Supplementary Materials), whereas further downstream ('MAGULA' station) (see also Figure 1) the C-P status gets improved in all monitoring parameters, including chlorides. Chlorides exceed the value of 70 mg·L^{-1} in four measurements out of eight conducted upstream, which turns to one exceedance out of five downstream in the 'MAGULA' station. These results are supported by Matiatos et al. (2023), who, based on stable water isotopes, found that organic pollution contribution from various point sources exceeded 70% in most Pinios River sites [41].

Nitrites are metastable anionic complexes, particularly toxic to aquatic biota. When present in waterbodies, in strong oxidized conditions, they turn, shortly after their formation, into nitrates, which are more stable in thermodynamic terms, constituting, therefore, a preferable form for aquatic ecosystems. The positive correlations of ammonium with BOD and ammonium with nitrite (Table S5, Supplementary Materials) provide evidence for organic matter mineralization and subsequent nitrification processes, respectively [40], driven by sufficient water oxygenation. The prevalence of nitrification processes in the basin is also supported by the findings of Matiatos et al. (2023) [41]. Our results at the LITHEO_DW station could support such an approach since it displays a high concentration of nitrites and ammonium concurrently. Finally, the diminishing of ammonium in late summer/autumn (Figure 4c) may be attributed to enhanced assimilation processes that favor its uptake by plants [41] or, in case of strong oxygen deficiency, to Anaerobic Ammonium Oxidation (Anammox), processing converting ammonium into dinitrogen gas (N_2), having as an intermediate stage nitrite formation [40,52–56].

Ammonia toxicity to aquatic life depends on water intrinsic quality characteristics, pH, and temperature values, which affect solubility. High ammonia concentrations incur fish tissue harm, toxic algal blooming, etc. Since 18% of the measurements revealed an exceedance of pH 9 due to increased photosynthesis (occurring all year round), massive fish deaths reported for Pinios River may be caused by ammonia toxicity, which may act concurrently with flow deterioration and oxygen deficiency in summer [57].

Water flow highly regulates the concentration of nutrients and determines the trophic state of river bodies. Due to climatic and water management issues, rivers in the eastern part of Greece show significant seasonal discharge variations and suffer from very low summer flow, even river types categorized as 'large' ones in terms of catchment area and rich water flow, i.e., RM-2, RM-3, RL [28,29]. Nevertheless, these river types are richer in water than the other river types and show a better C-P status. Rivers with a high seasonal flow, i.e., RM-1 and RM-4, are most susceptible to increased nitrate concentration as a result of flushing processes (Figure 6b). RM-4-type rivers demonstrated the highest nitrite values (Figure S3, Supplementary Materials). Poor hydrological season yields weak water currents with low dilution capacity to any point source pollution and favors locally the formation of small ponds with stagnated river water, where nitrifiers prevail [58,59]. RM-5 rivers, i.e., with a temporary flow regime, follow the same justification. RM-5 rivers are under environmental pressure due to desiccation and subsequent undesirable high pollutant concentrations, particularly $N\text{-}NH_4$, TP, and $P\text{-}PO_4$.

The improvement of the C-P classification status along the Pinios main course towards the river outflow is attributed to the positive effect of local spring inflows originating from two high-altitude mountain masses (i.e., Olympos and Ossa) surrounding the last course stage of the river (Figure 1) bluish-colored arrow on the right side.

The COVID pandemic lockdown, which lasted from 03/2020 until the end of the year, seems not to have affected water quality parameters despite an overall air quality improvement and lower pollutant inflows through wet and dry deposition as demonstrated elsewhere [60,61]. This is due to the fact that in the Pinios basin, ground sources of pollution are more significant compared to atmospheric inputs. On the other hand, although the amount of municipal wastewater effluents during the lockdown in many countries increased [61–63], no significant alterations were detected herewith regarding nutrients and dissolved oxygen.

The operation of WWTPs within large cities and agglomerations located upstream of sampling stations needs a more thorough investigation of wastewater treatment efficiency since any improper functionality significantly affects the water quality status. Our results, together with the observed recent increase in ammonium concentration in the outflow of the main river course [12], suggest that prompt measures should be taken to control and improve the operation efficiency of WWTPs within the basin. The same measures should be applied to food industries and animal breeding units.

Considering that phosphorous enriches river water mainly in summer, it may be concluded that organic pollution resulting from treated and untreated municipal wastes and industrial activities is the primary source of pollution in the Pinios basin, followed by agricultural land flushing. This result is supported by [41]. However, agricultural pollution is also substantial; the low ON contribution to TN is attributed to nitrogen inputs from N-fertilizers, which are still immense, despite the facts that the Thessaly basin has been designated as a Nitrate Vulnerable Zone with positive results (EC, 2002) and that nitrate levels in the river outflow have been improved in the recent decade [12,64–66].

Ongoing and future measures within the RBMPs should thus be high-priority target point sources of organic effluents and significantly intensify measures, e.g., connected to the nitrate directive, to more efficiently control N- and P-fertilizers in agriculture.

The excessive use of nitrogen-based fertilizers increases nitrate concentration in soils and surface waters and incurs aquifer nitrification. WWTP effluents, in combination with outdated irrigation techniques, contribute to a constant increase in chloride concentration in river water bodies and alter soil geochemistry balance and, therefore, crop yield. RBMPs should consider precision agriculture, deficit irrigation [67], restructuring of agriculture towards less water-demanding crops, and use of grey water, in addition to a better implementation of the nitrate-vulnerable zone principles. Moreover, prudent surface and groundwater management should fit with the circular economy to meet the requirements of goals 6, 12, and 14 of the United Nations agenda for sustainable development until 2030 [68].

The Pinios basin is vulnerable to floods caused by a combination of extreme meteorological events and hydromorphological alterations. Extreme weather event 'Daniel' struck certain areas in Greece (September 2023) with heavy, persistent rainfalls lasting for several days. It resulted in massive property damage in Thessaly because of the lack of adequate elevation to support rainwater runoffs, causing floods, landslides, uncontrolled agrochemical spread, and great loss of livestock potential. In the near future, the high-frequency occurrence of extreme phenomena compels local communities and stakeholders to proceed at a fast pace and conclude integrated water management plans. Awareness of surface water quality assures the applicability of proper sustainable practices, e.g., monitoring of groundwater quality, crop fertilizing policy, floods [69,70], nitrate vulnerable zones [42,71,72], and water supply sufficiency during periods of extreme events, such as prolonged drought and persistent floods [11,73–75].

FrameworkFuture WFD revisions based on United Nations Integrated Methodological Framework, along with the new Nature Restoration Law, are expected to strengthen initial provisions on water quality and ecological status assessment, enhance the involvement of stakeholders in the development of river basin management plans towards water sustainability pathways, and proceed towards NBS remedial actions [76–80], with special attention on adaptation and mitigation strategies of extreme weather events, to improve the status of this very important for the national economy, albeit highly degraded river.

The improvement of the C-P classification status along the Pinios main course towards the river outflow is attributed to dilution by local spring inflows originating from mountain masses surrounding the last part of the river course (Tempi area). However, this process may have recently weakened due to the dry spell period.

5. Conclusions

According to the results, the Pinios River is a recipient of multiple, inadequately treated, point, and dispersed pollutants.

Focusing on the C-P status of 30 river stations of the WFD monitoring network, 218 seasonal samples for the period 2018–2020 were analyzed, following nationally approved methods, to obtain the following main results: 86 samples, i.e., 40% of the total sample number, and 21 out of the 30 monitoring stations (i.e., 70%) revealed a lower than good C-P status, predominately as a result of elevated phosphate, TP, and nitrate concentrations.

Contrary to our understanding regarding the vast majority of Greek basins [25,50], phosphorous reaches the Pinios River not mainly as a result of agricultural soil flushing following hydrograph peaks but predominately due to organic pollution. This refers to bio-fertilizer application (in warm periods), inadequately treated municipal wastewater, and effluents from seasonal food industries operating in summer, in combination with organic matter mineralization processes. The latter, combined with nitrification (as indicated by [41]), may cause elevated nitrite, ammonium, and, in the case of eutrophication, ammonia concentrations. The aforementioned results may be interrelated with the observed massive fish deaths. The recent increase in ammonium concentration in the outflow of the river [12] is consistent with this concept. Thus, in the Pinios basin, organic pollution, combined with mineralization processes, seems to override the leaching of phosphate fertilizers from agricultural land during high flow events, underlying the high priority to control point source pollution in the basin. However, the long-term recent improvement of the river's nitrate quality [12] should not reassure water managers since the present study shows that in 83% of samples with lower than good C-P status, nitrate violates the good quality limit. Thus, programs of measures within the RBMPs should prioritize target point sources of organic effluents and significantly intensify measures to more efficiently control N- and P-fertilizers in agriculture, including NBS.

The COVID pandemic lockdown seems not to have affected water quality parameters through the improvement of atmospheric deposition due to the fact that in the Pinios basin, ground sources of pollution are significant compared to atmospheric inputs. Also, an increase in municipal wastewater effluents during the lockdown has not been detected.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/land13111959/s1.

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