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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 agri-cultural production, albeit severely degraded Pinios river, has been assessed for its Chemi-cal-Physicochemical status, based on the results of the National Monitoring Program for the years 2018-2020, considering 218 seasonal samples. Forty percent (40%) of the total samples, and 70% of the 30 monitoring stations revealed a lower than good Chemical-Physicochemical status based on the Water Framework Directive (2000/60/EC) limits, predominately as a result of ele-vated phosphate, total phosphorous and nitrate concentrations. Exceptionally, the Pinios river seems to be mainly affected by point sources of organic pollution, and secondarily by agricul-tural return flows and drainage processes, whereas dominant mineralization and nitrification processes control the concentration and speciation of Nitrogen and Phosphorus compounds. The coronavirus lock-down seems not to have affected aquatic quality significantly, whereas the im-provement Chemical-Physicochemical 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, urgent remediation measures in Pinios basin should target point sources of pollution and control agrochemicals, particularly focusing on adaptation strategies on extreme weather events.

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

1. Introduction

Clean and safe water for consumption is a fundamental human right, being essential for the protection of public health and the environment. Thus, surface and ground water quality management is an issue of high priority in the EU. 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, European's 96/61/EC Integrated Pollution Prevention and Control Directive (abbr. IPPC), 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, upon 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 are 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 which provoke wild fires, soil erosion etc., whereas anthropogenic pressure by means of industrial use, intense irrigation, human consumption, recreational activities exert stress to freshwater resources [14-15]. Thus, surface water bodies of Good Ecological Status (GES) are becoming scarce and problematic for consumption, changing surface and groundwater uses and affecting the local economy [15-16].

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 waste water discharges, exert immense pressures to surface and ground waters [12-22], while top soil 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.

Knowledge on river quality variations and of 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 chemical-physicochemical status (C-P status) of 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

Thessaly region (Figure 1) encompasses two major River Basins, namely Pinios River Basin (code EL0816) and Almyros – Pilio River Basin (code EL0817) [18]. Overall, seventy-two (72) surface water bodies were identified within Thessaly River Basin District with varying river typology [25-26]. Pinios River Basin is covered mainly by crops (51%), forests (34%) of various types and pasture (12%), while urban use (Figure S1, (Supplementary Material, SM) corresponds to 2% of the total area [18]. Eighteen (18) 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 of treatment installations is presented in Table S1, (SM) [27]. Officially, only one (1) WWTP located in Karditsa was designated with operational problems and performed non conformity against EEC 91/271 Directive prerequisites [28], 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 (SS). In Thessaly are located six designated Industrial Areas (IA), three of which are in vicinity to the city of Volos [29]. Volos IAs do not affect upon Pinios river water bodies. The other two of our interest 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 [30]. 'Plastira' Reservoir, transferring water from Acheloos River Basin, covers supplementary irrigation and human consumption needs of Karditsa municipality administrative area [18].

The Pinios basin annually receives hundred thousand tons of fertilizers, thousand tons of pesticides, and is receiving high organic waste water loads from partly untreated municipal and agro-industrial effluents [31-32]. The latter caused a worsen of ammonium quality during the last decade, despite a general improvement of its C-P status [12]. Shallow groundwaters illustrate dramatic nitrate levels, making them unsuitable for human consumption [33], despite the fact that the basin has been designated a nitrate-vulnerable zone.
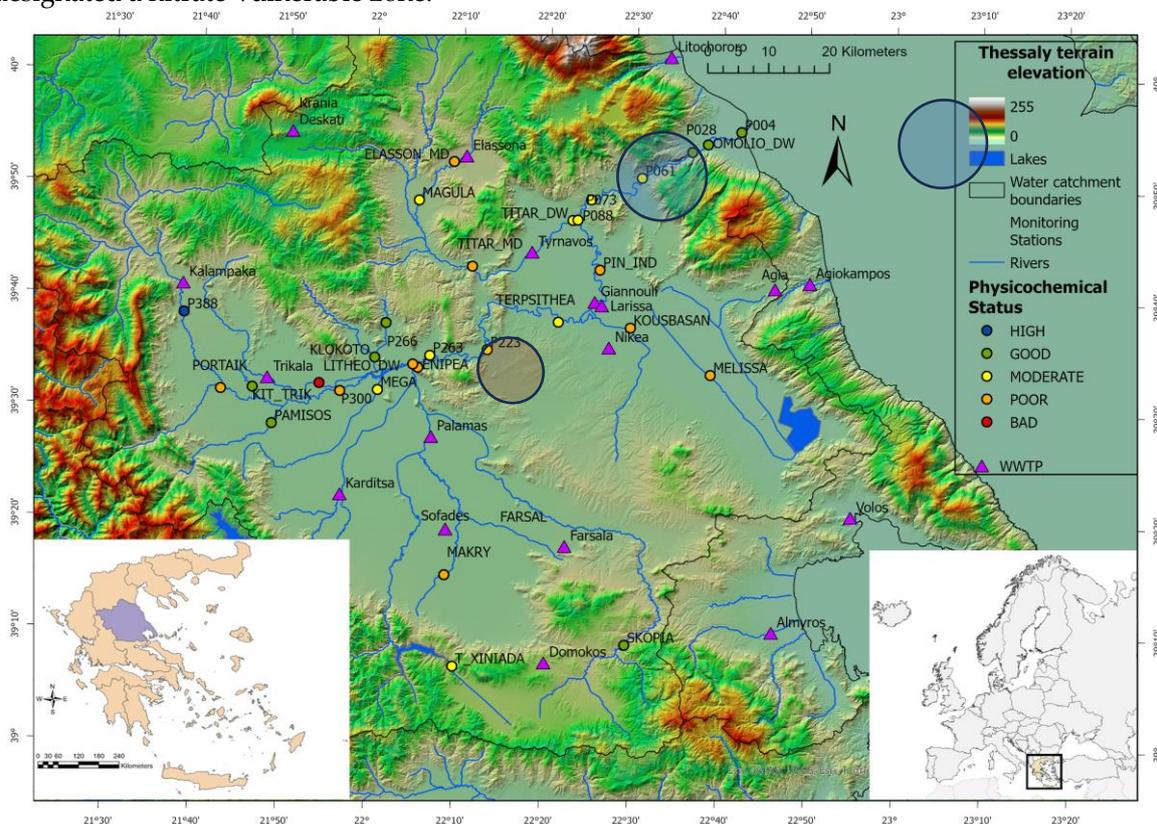

Figure 1. Terrain elevation of Pinios river catchment and physicochemical status of quality monitoring stations (5-quality classes) [27, 34]. Sampling stations in cycles are mentioned in the text.

Member States share particular surface water body types and collected data, following the conclusion of Geographical Intercalibration Groups (GIG). 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 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 S4, SM).

2.2. Sampling and Analysis

In this study, water quality data from Thessaly rivers from the period 2018-2020 were considered, 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 (Hellenic Centre for Marine Research), according to the WFD provisions [36]. Seasonal data regarding nutrients (nitrates, nitrites, ammonium, phosphates), turbidity, dissolved oxygen, water temperature, electric conductivity, chloride, and pH have been deployed from the WFD database of the Hellenic Centre for Marine Research, 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

All data derived by means of field sampling and lab analyses (for sampling and laboratory analysis procedures please refer to [37]), underwent data processing by combined data analyses techniques. Each sampling station was assigned a unique id code and a brief description.

Furthermore, Pinios tributaries' network was classified in accordance with Med-river bodies intercalibration exercise preceded to define type-specific reference conditions [25-26], as given below in Table 1.

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 S2, SM) [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

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 (RBMP). 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], (Table S1, SM) and the overall average score provided the final status C-P classification (Table S2, SM), [38]. Dissolved Inorganic Nitrogen (DIN) comprises the sum of (N-NO$_3$), (N-NH$_4$) and (N-NO$_2$). TN, which is the sum of DIN and nitrogen bound to organic matter (ON), determined the trophic state [39-40] (Table S2, SM).

Significant information is received from cross-correlation matrices. Correlations were tested, pairwise, between measured parameters making use of mean concentration of all involved monitoring stations (Table S5, SM). In general, weak correlations prevailed as a result of overlapping, opposing processes [41] running in the Pinios river basin (e.g. photosynthesis versus respiration, nitrification versus denitrification) [42]. 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 winter 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 five meteorological stations (Table 5) were recorded and interrelated to the obtained results to quantify the degree of influence (National Observatory of Athens, NOA), (Figure S2, SM) [43].

3. Results

3.1. Temporal Variations of 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 S3, SM) of (NOA in the region of interest) [43]. Intense rainfall recorded in December 2017 and winter 2018 (Figure 3a) is reflected in temporarily increased turbidity measurements, via an increase of turbidity physical index (NTU) (Figure 3b). Persisting precipitation affects significantly 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 2b; Table S2, SM). 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.

Ammonium median value appeared to lie steadily within the 'Good Status' band in all years studied (Figure 2a) with median and average values lying closely in 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 lower 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.

The boxplots for 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 2c). The TP median values in the years 2018 and 2019 were below the Good/Moderate boundary and the average value lay within 'Poor Status' band (see Table S2, SM). In 2020, the highest TP concentration values were reported with more than 40% being classified as of poor or bad quality.
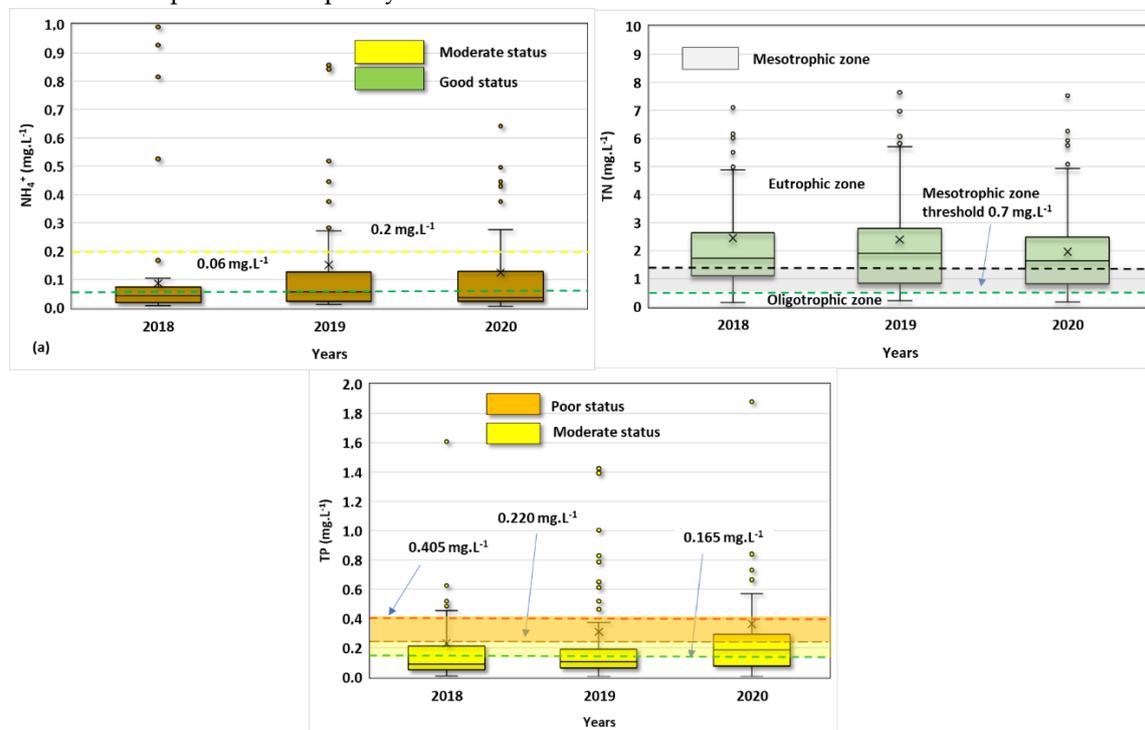

Figure 2. (a) Variation of ammonium measurements in the years 2018-2020. Green and yellow dashed lines denote 'Moderate' and 'Good' status thresholds, respectively [34] **(b)** Variation of TN measurements in the years 2018-2020. The grey colored band denotes the mesotrophic state area. [38-39] **(c)** TP measurements in the years 2018-2020. Green, orange and red dashed lines denote 'Good', 'Poor' and 'Bad' status thresholds, respectively [34].

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 3c), denoting the prevalence of 'good' and 'high' oxygen status according to Table S2, SM. In addition, only 5% of DO measurements revealed hypoxic conditions, i.e. concentrations below 3 mg/l. Finally, dissolved oxygen concentration was inversely correlated to water temperature as verified by the cross-correlation (Figure 3d; Table S4, SM).
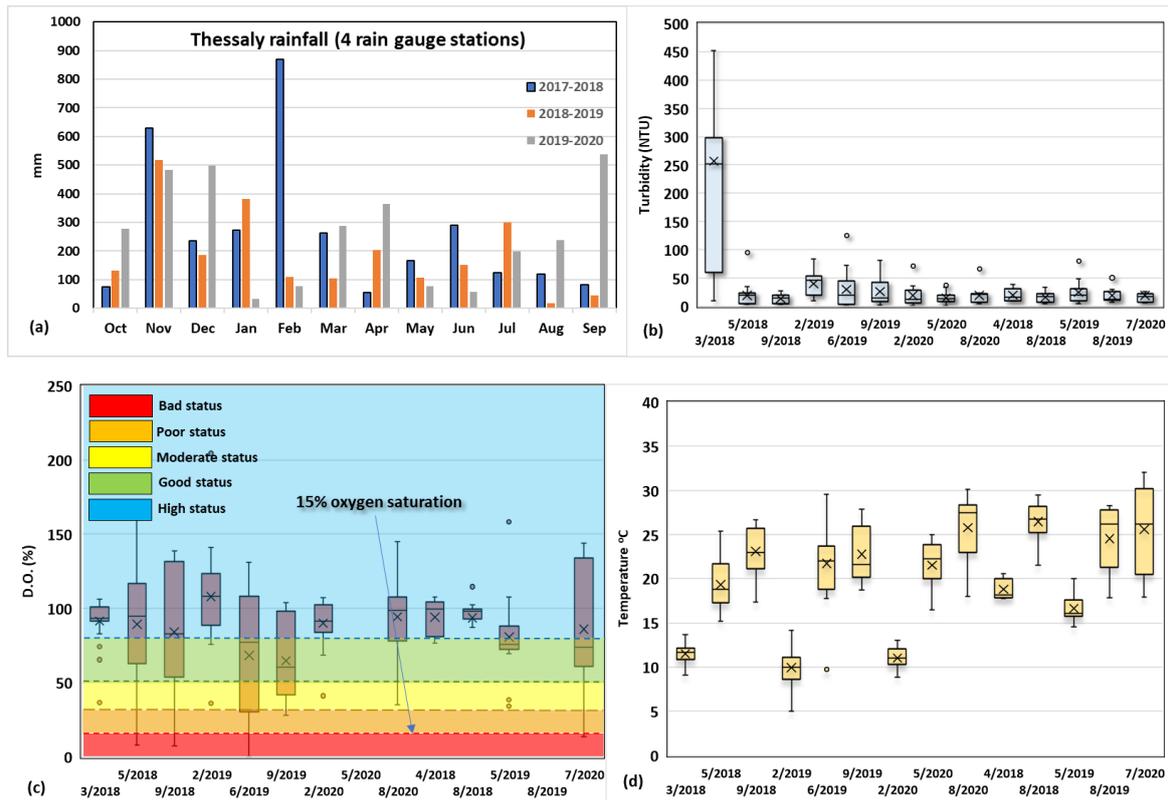
Figure 3. (a) Variation of seasonal rainfall in 2018-2020, based on data collected from four rain gauge stations (Table 4, SM), [43] **(b)** Turbidity measurements at all monitoring stations in Pinios basin (2018-2020) at predefined sampling periods **(c)** Dissolved Oxygen saturation in river waterbody and **(d)** temperature, measured at all monitoring stations in Pinios basin (2018-2020) at predefined sampling periods [44].

Apart from 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).

Only in August 2018 and 2019, river water bodies sustain a "Good Nitrate Status" (Figure 4b) (see Table S2, SM). 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 S5, SM), and especially TP and Cl-, present a positive correlation with BOD. The mean value of the fraction (organic phosphorus/TP) estimated to be 0.31. Apart from August 2020, river waterbodies' nitrite quality lies below 'Bad status' zone (Figure 4d; Table S2, SM). The majority of the measurements lies within 'moderate/poor status' zone.
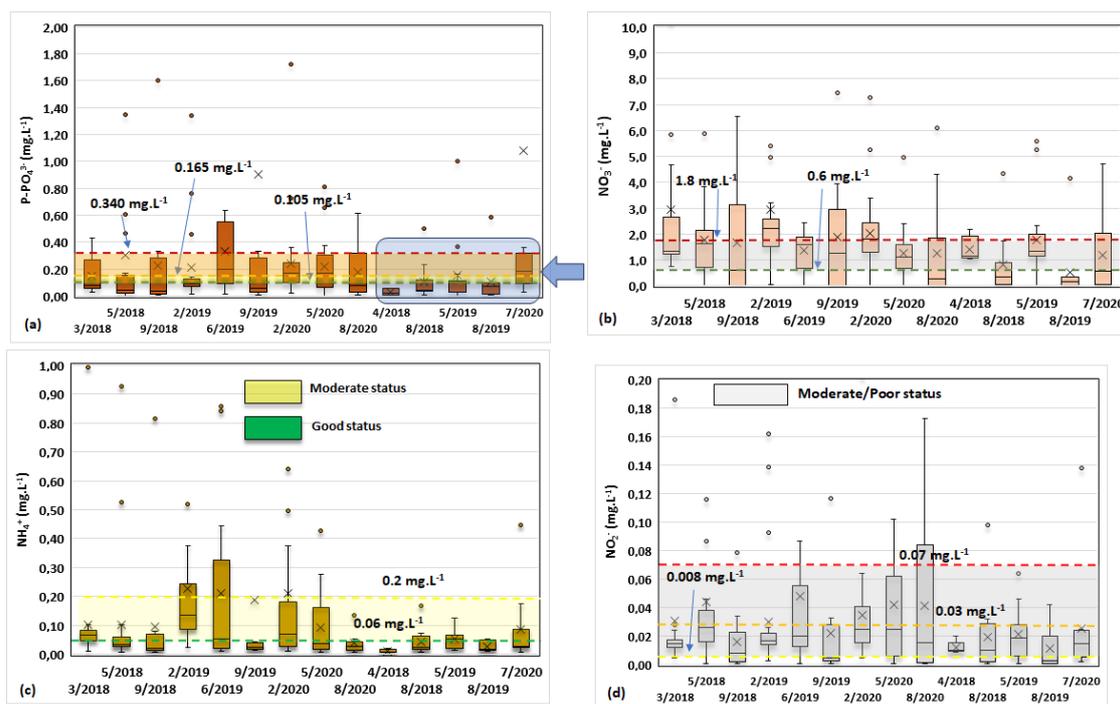
Figure 4. (a) Orthophosphates conc. fluctuation (2018-2020). The bluish frame corresponds to the COVID pandemic lock down period in Greece [34]. **(b)** River waterbodies nitrates conc. measured at all monitoring stations in Pinios basin (2018-2020) at predefined sampling periods. Green Dashed line defines the boundary value between good/moderate status [34]. **(c)** Ammonium and **(d)** nitrites concentrations measured at all monitoring stations in Pinios basin (2018-2020) at predefined sampling periods. Quality classes according to [34].

3.2. Spatial variations of chemical-physicochemical status

Elassonitis, a tributary of Pinios river, downstream 'Elassona' site WWTP at 'ELASSON_MD' monitoring station (Figure 1), demonstrates high TP, moderate ammonium values, elevated chloride concentration (4 out of 8 measurements exceed 70mg.L^{-1}, the upper accepted level for unconcerned plant growth after irrigation, [45]), and a 'poor' C-P classification. A further downstream station named 'MAGULA' (Figure 1) 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 S6, SM), seems to operate smoothly, i.e. within EEC 91/271 guidelines [27-28].

The last three sequenced monitoring stations located just before the deltaic zone 'P004', 'OMOLO_DW' and 'P028' (Figure 1), 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, WWTP of Karditsa was recorded by the competent Greek ministry (Hell. Min. Env. Ener., 2024) as non-compliant to EEC 91/271 regulated limits, as regards (BOD5, COD). Therefore, there is strong evidence that sampling results from the above given monitoring station are negatively affected by inadequate urban wastewater treatment.
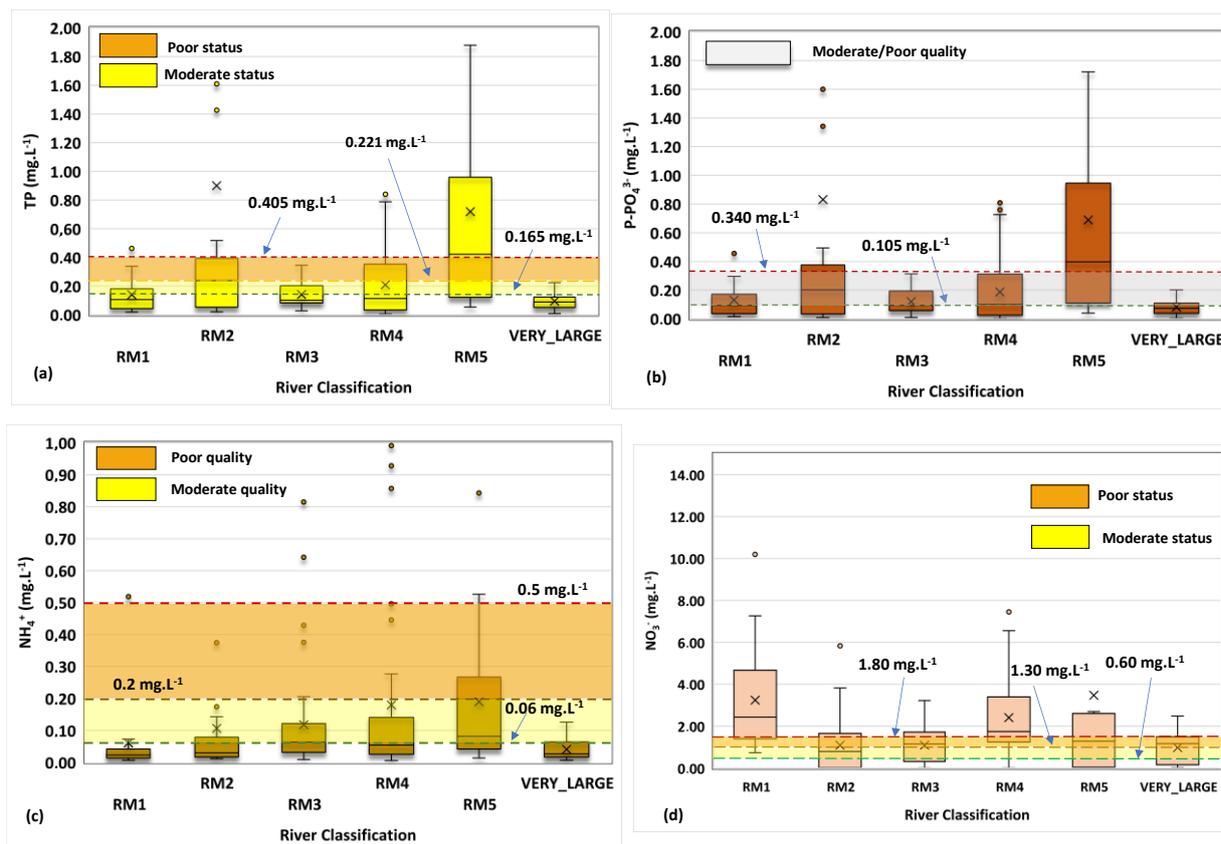
Figure 5. (a) River waterbodies total phosphorus concentration [34] measured at all monitoring stations in Pinios basin (2018-2020) at predefined sampling periods **(b)** Overall orthophosphate anions conc. [34] **(c)** ammonium cations concentration **(d)** Nitrates conc. measured within 2018-2020 period for various classified Med-river types. Quality classes [34].

Regarding TP, 'RM-5' rivers demonstrate significant median values, considerably higher than the other river types (Figure 5a). 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-NO3 measured values (Figure 5d).

RM-3 and i.e. RL-1 and RL-2 type (see Table S4, SM) are all rich in water and display the best quality as regards 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 bound to organic matter ON. RM-2 medium size streams and RM-3 very large rivers display almost the same median (Figure 6b).
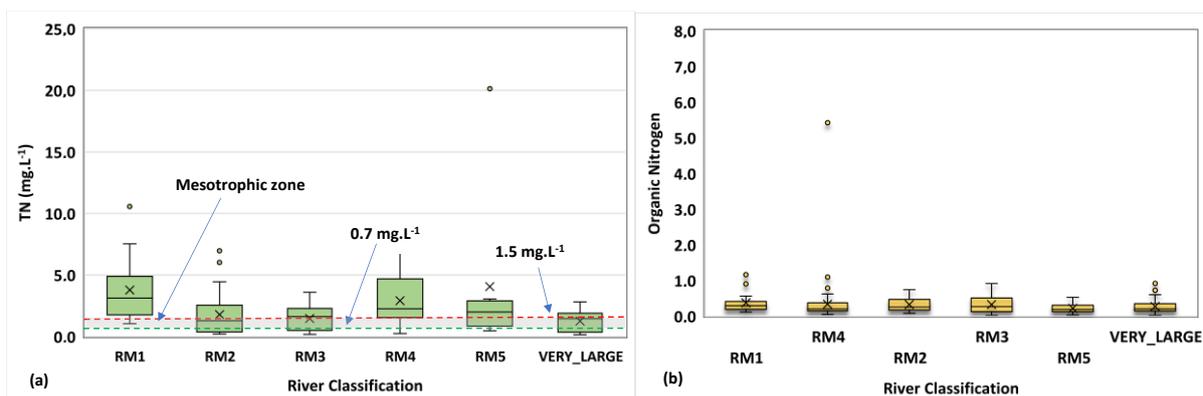
Figure 6. (a) Overall total nitrogen concentration. Trophic status classification after [38-39] **(b)** Organic nitrogen in different river types.

3.3. Management Issues

In Figure 7, an overall assessment of the C-P status in 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, collected from thirty (30) monitoring stations, classified as 'Good Status', fifty-seven (57) as 'Moderate' and twenty-nine (29) as 'High Status' samples. Sixty two 62% of the measurements achieve a C-P satisfactory status. That entails extensive rehab actions to be taken for the C-P improvement.

Moreover, 86 out of 218 measurements, i.e. 40%, revealed a lower than good C-P status. From this total, only the 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 from nutrients are the sites depicted in Table 2.
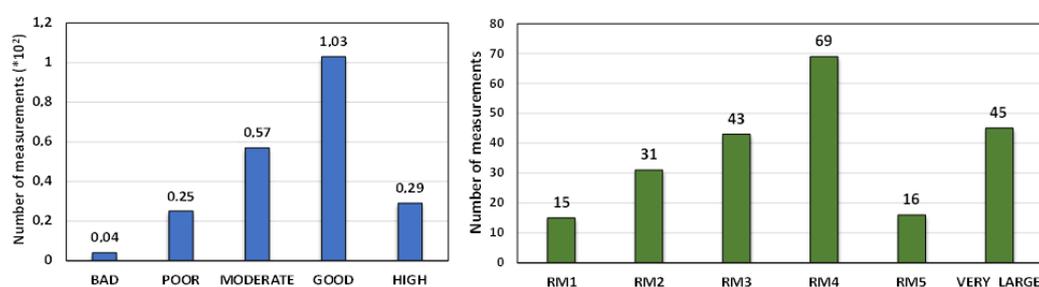

Figure 7. The physicochemical status of the operated monitoring stations at Pinios river catchment in Thessaly and Sterea Ellada in central Greece.

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-PO₄ limit exceedance	N-NH₄ limit exceedance	N-NO₃ 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, 2) monitoring stations demonstrated C-P status lower than 'good' in 86 seasonal measurements, i.e. a percentage of 70%. DO values has similar levels of 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.

Despite of high organic waste water inputs in the Pinios basin, 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 to 37.1 [46], whereas the average ON percentage in the almost undisturbed Krathis river basin reaches 76.5 [47].

4. Discussion

In Pinios basin, DO values showed that surface waters are mostly under oxidizing conditions, despite the impact of organic waste waters. Dissolved oxygen concentration was inversely correlated to water temperature as verified by the cross-correlation matrix (Table S5, SM) and literature [48]. In addition, DO revealed negative correlations with BOD and TP (Table S5, SM) 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 of 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 [41, 49-50], deteriorating oxygen concentrations and violating good oxygen quality in half of the measurements carried out.

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 [51]. Considering that the Pinios basin is covered by over 24% by irrigated cultivations [52] and that vast cropland areas are in proximity with 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 indicate (Table S5, SM). 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 [42]. Most of the samplings regard RM-4 type rivers which indicates that seasonal phenomena are most probably C-P classification controllers.

In Pinios River, orthophosphate is the nutrient species which 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 [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 use, as a recycled byproduct from local vivid breeding farm activities (i.e. pigs, cattle, poultry) applied in warm periods, together with inadequately treated municipal waste waters 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 leaching of phosphate fertilizers from agricultural land during high flow events. Similarly, WWTP malfunctioning, along with seasonal food industry and livestock activities give rise to TP, ammonium and chloride (since Cl$^-$ is contained in urea), as the positive correlation between TP, ammonium and chloride with BOD indicates. 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 S6, SM**), whereas further downstream ('MAGULA' station), the C-P status gets improved in all monitoring parameters, including chlorides. Chlorides exceed the

value of 70mg.L^{-1} in four measurements out of eight conducted upstream which turns to one exceedance out of five downstream in 'MAGULA' station (Tables 2, 8). 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 [42].

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 more preferable form for the aquatic ecosystems. The positive correlations of ammonium with BOD and of ammonium with nitrite (Table S5, SM) provide evidence for organic matter mineralization and subsequent nitrification processes, respectively [41], driven by sufficient water oxygenation. The prevalence of nitrification processes in the basin is also supported by the findings of Matiatos et al. (2023) [42]. Our results at LITHEO_DW station could support such an approach, since it displays high concentration of nitrites and ammonium concurrently (Table S5, SM). Finally, the diminishing of ammonium in late summer/autumn (Figure 4c) may be attributed to enhanced assimilation processes that favor its uptake by plants [42] or, in case of strong oxygen deficiency, to Anaerobic Ammonium Oxidation processing converting ammonium into dinitrogen gas (N$_2$), having as an intermediate stage nitrites formation [41, 53-57].

Ammonia toxicity to aquatic life depends on water intrinsic quality characteristics, pH and temperature values, which affect solubility. High ammonia concentration incurs fish tissue harm, toxic algal blooming etc. Since 18% of the measurements revealed exceedance of pH 9, due to increased photosynthesis (occurring all year round), massive fish deaths reported for Pinios River may be caused to ammonia toxicity which may act concurrently to flow deterioration and oxygen defficiency in summer [58].

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 [25-26]. 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 nitrates concentration as a result of flushing processes (Figure 6b). RM-4 type rivers demonstrated the highest nitrite values (Figure 5d). 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 are prevailing [59-60]. RM-5 rivers, i.e. with 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-NH$_4$, TP and P-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 springs 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 lock down, 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 [61-62]. This is due to the fact that in Pinios basin ground sources of pollution are more significant compared to atmospheric inputs. On the other hand, although the amount of municipal waste water effluents during the lock down in many countries increased [62-64], no significant alterations were detected herewith as regards to 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 long-term increase in ammonium concentration in the outflow of the main river course [12] suggests that urgent measures should be taken to control and improve the operation efficiency of

WWTPs within the basin. Same measures should be applied for food industries and animal breading 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 Pinios basin, followed by agricultural land flushing. This result is supported by [42]. However, agricultural pollution is also substantial; the low ON contribution to TN is attributed to N inputs from N-fertilizers, which are still immense, despite the facts that the Thessaly basin has been designated as Nitrate Vulnerable Zone with positive results (EC, 2002) and that nitrate levels in the river outflow have been improved in the recent decade [12, 65-67].

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

The excessive use of nitrogen-based fertilizers increases nitrates concentration in soils and surface waters and incurs aquifers nitrification. WWTPs effluents in combination with outdated irrigation techniques contribute to a constant increase of chloride concentration in river water bodies and alter soil geochemistry balance and therefore crop yield. River Basin Management Plans should consider precision agriculture, deficit irrigation [68], restructuring of agriculture towards less water-demanding crops and use of grey water, additionally to a better implementation of the nitrate-vulnerable zone principles. Moreover, prudent surface and groundwater management should feet with circular economy to meet the requirements of goals 6, 12 and 14 of the United Nations Agenda for Sustainable Development until 2030 [69].

The Pinios basin is vulnerable to floods caused by a combination of extreme meteorological events and hydromorphological alterations. Extreme Weather Event 'Daniel' stroke certain areas in Greece (Sept. 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 with 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, crops fertilizing policy, floods [70-71], nitrates vulnerable zones [42, 72-73] and water supply sufficiency, during periods of extreme events, such as prolonged drought and persistent floods [11, 74-76].

Future WFD revision based on United Nation's Integrated Methodological Framework, along with the new Nature Restoration Law, are expected to strengthen initial provisions on water quality and ecological status assessment, to enhance the involvement of stakeholders in the development of river basin management plans towards water sustainability pathways, and proceed towards NBS-based remedial actions   [77-81].

5. Conclusions

Pinios river basin is the vast part of Greece's agriculturally most productive basin, the Thessaly basin, with over a half of million inhabitants. The river is a recipient of multiple, inadequately treated, point and dispersed pollution sources, suffers water shortages due to immense ground- and surface water abstraction for irrigation and is prone to climate change/variability induced droughts and floods. It is thus not surprising that the Pinios basin has been classified among the most degraded in Europe [22].

Focusing on the C-P status of 30 river stations of the WFD monitoring network, 218 seasonal samples for the period 2018-2020 were analysed, 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, preodominately as a result of elevated phosphate, TP and nitrate cocentrations.

Contrary to our understanding regarding the vast majority of Greek basins [31, 51], phospohrous reaches the Pinios river not mainly as a result of agricultural soil flushing following hydrograph

peaks, but predominately due to organic pollution. This referes to bio-fertilizers application (in warm periods), inadequately treated municipal waste waters and effluents from seasonal food industries operating in summer, in combination with organic matter mineralization processes. The latter, combined with nitrification (as indicated by [42]), may cause elevated nitrite, ammonium, and in case of eutrophication, ammonia concentrations, which may be interrelated with the observed massive fish deaths. The recent long-term increase in ammonium concentration in the outflow of the river [12] is consistent with this concept. Thus, in Pinios basin, organic pollution, combined with mineralization processes seem to override leaching of phosphate fertilizers from agricultural land during high flow events, underlying the urgent 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 this study shows that in 83% of samples with lower than good C-P status, nitrate violates   good quality limit. Thus, Programms of Measures within the RBMPs should urgently 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 lock down seems not to have affected water quality parameters through the imrovent of atmospheric deposition due to the fact that in Pinios basin ground sources of pollution are significant compared to atmospheric inputs. Also, an increase of municipal waste water effluents during the lock down has not been detected.

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

Future WFD revision based on United Nation's 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-based remedial actions, 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.

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