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POLLUTION SOURCES IN WATER OF YOUNG RESERVOIRS - CASE OF ILARION HYDROELECTRIC DAM, GREECE

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Abstract

Evaluation of spatial/ temporal water quality data at reservoirs has shown differences after the dam construction as well as long-term changes of water chemistry. One of the most recent reservoirs created in Europe is Ilarion Reservoir in Western Macedonia – Greece (2012). In this work, the water physicochemical characteristics of this young reservoir and the spatiotemporal water quality variation of the feeding river and its main tributaries have been studied, and statistically interpreted. The aqueous system of the young reservoir after two years of formation does not seem to have reached its stabilization age but a stabilization tendency appears at some quality parameters. The dissolution of plant residues covering the flooded areas and the water volume changes affected the water quality, while excesses of legislation's limits for some parameters have been observed. The most affected parameters, remaining at high levels are TKN, ammonia, nitrite nitrogen and color. The feed water quality is generally within the legislation's limits with the exception of nitrite and ammonium nitrogen parameters which exceed the maximum permissible legislation's limits and are the main pollution sources of the young reservoir. Monitoring these parameters is necessary to determine if the observed excess values could lead to eutrophic conditions and toxic habitat for fishes. The statistical analysis indicated some significant parameters responsible for large variations in water quality and allowed the identification and apportionment of pollution sources as an aspect of the temporal/spatial variations in water quality, indispensable for effective water quality management.

Key words: young reservoir, statistical analysis, water quality

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1. Introduction

According to UNESCO's guidelines, freshwater reservoirs are used to regulate flow for many purposes, including: water supply, irrigation, aquaculture, flood mitigation, drought protection, navigation, hydropower etc. The construction of an artificial reservoir has high financial, environmental and social impacts and is imperative to understand the interactions among them (Kornijów, 2009; Wu and Chen, 2013; Zhao et al., 2012). Environmental impacts are of high significance because changes in terrestrial ecosystems can affect climate, soils, vegetation, water resources and biodiversity which are closely linked to the sustainability of socio-economic development (He et al., 2003; Kellogg and Zhou, 2014; Tullos, 2009). Furthermore, it is well known that the conversion of terrestrial land to an aquatic area for creating a reservoir is a major issue with regard to greenhouse gas (GHG) emission and carbon cycle change (Guerin et al., 2008; St-Louis et al., 2000; Teodoru et al., 2011). Anything that impairs the reservoirs potential uses has direct and noticeable cost (UNESCO/IHA, 2008).

Studies on reservoir water quality have highlighted changes of the chemical and biological

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water characteristics, for many years since the beginning of water storage. Immediately after dam filling, some studies reported rapid deterioration of water quality (Bonanomi et al., 2014; Deng et al., 2017; Richard et al., 1997; Staškraba et al., 1993). The reservoirs formed are frequently viewed as unstable ecosystems, that have features of the original river (lotic) and features of the new lentic condition (decomposition of the submerged vegetation, higher water retention time, stratification, higher depth) (Tundisi, 1990). After the filling, a complex process of reservoir ageing starts with a rate depending on the water residence time. A "mature" stage is achieved after stabilization of all components and processes within the ecosystem, from abiotic to biotic ones and from microorganisms and primary producers to the highest trophic link (Straškrábová et al., 2005). Maturity is an inherent characteristic of reservoir aging, regardless of human interference, reservoir area or number of species (Gubiani et al., 2011). Independent variables such as rainfall, winds and presence of tributaries have significant effect on reservoir water quality. The increasing anthropogenic activities alter the trophic status of the ecosystem (Carpenter et al., 1998; Hoeinghaus et al., 2008; Jarvie et al., 1998; Villanueva et al., 2006), degrade surface waters and impair their use for drinking, industrial, agricultural, recreation or other purposes. Water quality in reservoirs is highly dependent on the organic matter and nutrient load from rivers and tributaries. Excessive nutrient load leads to algal bloom that increases water treatment cost, and may prevent human and animal water consumption, if toxin-producers are present in the phytoplankton community (Marcé et al., 2008). Algal bloom also has great impact on recreational uses, impoverishment of fish community, and worsening of the social perception of the water body (Larson, 2008).

Water quality parameters that have shown remarkable change and attest gradual deterioration after the construction of reservoirs, were Biochemical Oxygen Demand (BOD), nitrate nitrogen and ammonia nitrogen (Asante et al., 2005; Bonanomi et al., 2014; Bosque-Hamilton, 2004; Gonzalez et al., 2012; Palma et al., 2014; Stanley and Doyle, 2002). Also, after filling a new reservoir, dissolved organic carbon and nutrients (nitrogen, phosphorous, etc.) are released in the water column from the decomposition of the vegetation debris (Bonanomi et al., 2014; Wetzel, 2001). The intensity of this process is controlled by temperature (Dang et al., 2009), oxygen level (Chabbi and Rumpel, 2004), nutrient availability (Xie et al., 2004) and pH (Carpenter et al., 1983). Immediately after dam filling, some studies reported deterioration of water quality with low oxygen level, high turbidity and a release of nutrients into the water body (Bonanomi et al., 2014; Richard et al., 1997; Staškraba et al., 1993).

Evaluation of spatial and temporal water quality data at reservoirs has shown differences after dam construction as well as long-term changes. In view of the spatial and time variations in the hydrochemistry of surface waters, regular monitoring programs are required for reliable estimates of water quality (Singh et al., 2004). Water quality monitoring is a helpful tool not only to evaluate the impact of pollution sources but also, to ensure an efficient management of water resources and protection of aquatic life (Strobl and Robillard, 2008). Additionally, monitoring is essential in order to create reliable and representative data bases prerequisite for applying different statistical techniques such as standard statistical tests, exergy analysis, single index, gray correlation etc. (Awadallah et al., 2011; Chen and Ji, 2007; Dai et al., 2010; Chen, 2012; Sun et al., 2013). Statistical techniques facilitate the interpretation of complex data matrices for better estimation of water quality and ecological status of the studied systems (Varol et al., 2012). These statistical methods also assist the identification of possible factors/sources that influence water systems and offer a valuable tool for reliable management of water resources as well as rapid solutions to pollution problems (Hering et al., 2010; Palma et al., 2014; Shrestha and Kazama, 2007; Simeonova et al., 2003; Varol and Şen, 2009; Varol et al., 2012).

Consequently, researchers and managers involved in dam construction face the continual difficult question about what water quality (short-term and long-term) will be after construction in a given location and about the main quality problems that will arise. This must be taken into account during the dam's project design period as well as during the water body management (Marcé et al., 2010). The assessment of reservoir's water quality is imperative in order to ascertain the contamination cases that may be confronted and the inherent impacts on human activities (Carpenter et al., 1998).

In the Mediterranean Basin examples of studies on reservoirs water quality during their transitional period from lotic to lentic conditions are scarce (Bonanomi et al., 2014). One of the most recent reservoirs created in Europe is Ilarion Reservoir in Western Macedonia – Greece which was formed in 2012 from the impoundment of Aliakmon River water. The reservoir will have multiple usages, including hydroelectric power production, irrigation and recreation. In the present work, the water quality of the newly formed Ilarion Reservoir during the period 2012-2014 is studied. This is the first monitoring program executed in the young reservoir and is covering the transitional period of the reservoir from lotic to lentic conditions.

The main objectives of the present study were: (1) to assess the spatial and temporal variations of reservoirs water quality during these first years of its formation (2) to characterize the present status of the water body (3) to identify the chemical parameters of the ecosystem most affected by the change from lotic to lentic conditions, (4) to identify the various sources of contaminants responsible for the water deterioration.

To achieve these goals physical and chemical analysis were performed in the Ilarion reservoir during the study period as well as the water quality variation of Aliakmon feeding river and its main tributaries for a period of twenty years was studied and statistically interpreted.

The results of this study will consist a reliable database useful for future studies, provide scientific basis for more effective management of reservoir pollution problems and may prove to be an important water resource management tool for other similar reservoirs.

2. Materials and methods

2.1 Study area

The Ilarion reservoir is located in north-western Greece and is formed from the impoundment of Aliakmon River water at “Moni Ilarion” location by a hydroelectric dam. It is the first dam met, in the direction of the river’s flow, and the youngest of the totally four reservoirs (Mimikou and Baltas, 1997) constructed on Aliakmon River (Fig. 1). It is an artificial Mediterranean reservoir with a surface area of 21.9 km^2 and a maximum depth of 100m and a volume of $412 \cdot 10^6$ m^3. The lake water feed is mainly from the upstream part of Aliakmon River (4050 km^2 catchment area) and secondly from tributaries of lake’s catchment area (662.25 km^2 area).

A detailed investigation of the Aliakmon River physico-chemical characteristics was conducted by Ministry of Agriculture during 1980-1997 (Ministry of Agriculture, 1998). Zarfdjian et al. (2000), studied the zooplankton abundance in the river, which was found to be typical of small rivers with seasonal variations highly depended on pH, dissolved oxygen and phosphorus variations. Skoulikidis et al. (2002) examined the biotic and physicochemical parameters of the river (July 1996-March 1997) and classified water quality between “high” and “moderate”. Hellenic Centre for Marine Research (HCMR, 2009) (study period September 2007-October 2007) classified water quality as “high” and determined the nutrients from agricultural livestock activities as the most possible cause of quality degradation.

The Ilarion reservoir filling resulted in flooding large terrestrial and natural aquatic ecosystems areas (Table 1). Up to 21.9 km^2 of reservoir bottom consist of flooded mature forest with various degrees of canopy cover, non-forest soil, and rivers.

During the study period temperature and precipitation ranged at the same level as previous years. An average atmospheric temperature of 16ºC ranging from -1.2 ºC in January to 25.3 ºC in July was recorded. The average monthly precipitation for 2011/2012 was 40mm and for 2013/2014 was 50 mm.

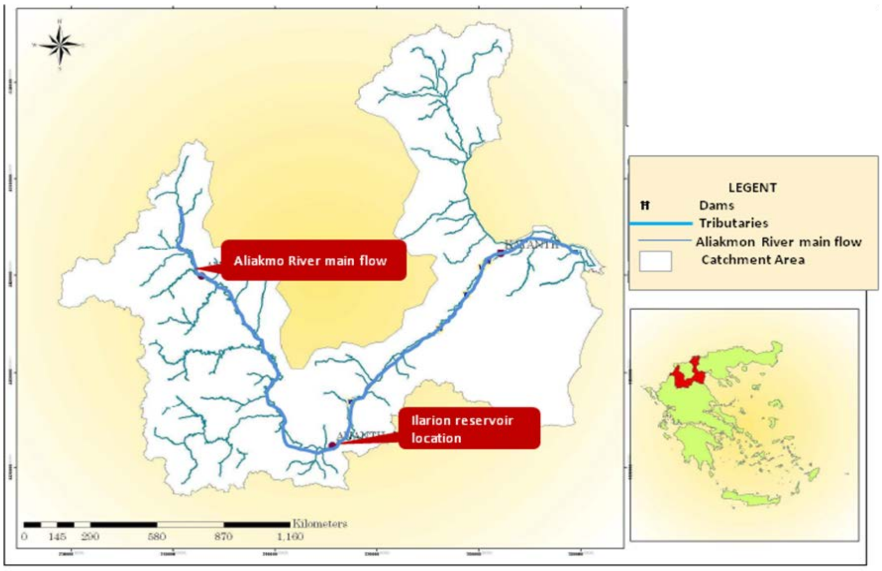


Fig. 1. Aliakmon River flow and its tributaries, catchment area and Ilarion reservoir location

Table 1. Total flooded area and percentage according to degree of canopy cover and terrestrial ecosystem

Terrestrial ecosystem, Landscape type	***Total flooded area and percentage according to degree of canopy cover and terrestrial ecosystem***					
Landscape	Minimum (10-40%)		Mean (40-70%)		Maximum (70-100%)	
Rivers (hectares)	5.068	23.01%	5.068	23.01%	5.068	23.01%
Non-forest soil and soil remained according to the mean degree of canopy cover (hectares)	13.4768	61.19%	11.6798	53.03%	9.8828	44.87%
Forest (hectares)	3.4792	15.80%	5.2762	23.96%	7.0732	32.12%
Total flooded area	22024	100%	22024	100%	22024	100%

2.2. Sampling and analysis

Previous monitoring programs of Aliakmon River, reservoirs' geometrical characteristics (shape, length, and depth) and safe accessibility were the criteria taken into account for the final establishment of sampling sites. Three sampling sites were selected to represent the upper (Karpero), middle (Elati), and lower (Moni Ilarion) part of reservoir. A fourth site below the dam (Exit) was chosen as downstream the dam, many concentration changes of water constituents are expected (Kurunc et al., 2006).

Forty-five samples were collected at twelve different sampling field trips. Two samples were collected during the end of flooding period (autumn 2012), three immediately after filling (winter 2012) and seven after one year (winter 2013-2014, spring 2014). In Fig.2 the sampling sites and Ilarion Reservoir location are depictured. The samples were collected according to ISO 5667-4 (ISO, 1987), ISO 5667-6 (ISO, 2005) and the relevant procedures of ISO 17025 (ISO 17025, 2005). During sampling, dissolved oxygen (DO) concentration and saturation of surface samples according to 4500-O G, (APHA, 2005) and temperature variation in relation to water depth were measured. Water samples were stored in polyethylene bottles and transported to the laboratory in a cooler at 4ºC.

In this study, for selecting the monitoring analysis parameters Directive 2006/44/EC for "quality of fresh water needing protection or improvement in order to maintain fish life", Directive 79/869/EEC for "surface water intended for drinking water", previous monitoring programs of Aliakmon River and relative literature were taken into account.

The measured parameters were pH according to 4500-H^+ (APHA, 2005), conductivity according to 2510 B (APHA, 2005), Chemical Oxygen Demand (COD) according to 5220 COD-C (APHA, 2005), Total Khendalh Nitrogen (TKN) according to 4500-Norg C (APHA, 2005), total ammonium nitrogen according to 4500-NH_4^+ F (APHA, 2005), nitrite nitrogen according to 4500-NO_2^- B (APHA, 2005), nitrate nitrogen according to 4500-NO_3^- B (APHA, 2005), alkalinity according to 2320-B (APHA, 2005), suspended solids according to 2540-TSS D (APHA, 2005), turbidity according to 2130-B (APHA, 2005) and color according to 2120-B (APHA, 2005).

Sample analysis was conducted in the accredited (according to ISO 17025) "Environmental Chemistry and Wastewater Treatment Laboratory", Department of Environmental Engineering, Technological Education Institution of Western Macedonia, Greece. Standard methods were applied using high purity control samples, calibrated instruments and certified volumetric glassware.

2.3. Statistical analysis

Water pollution sources in the young reservoir were identified by statistical analysis of feed water and reservoir water.

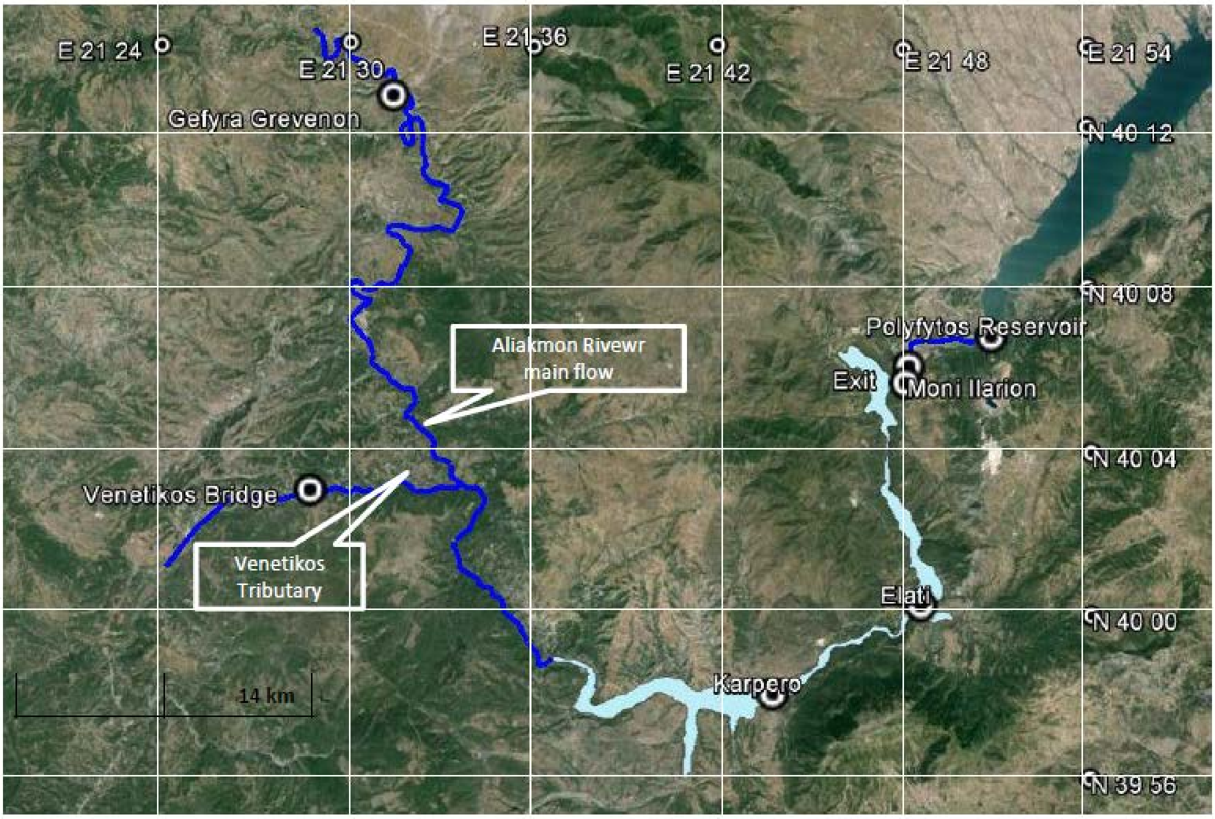


Fig. 2. Location of the young Ilarion Reservoir and sampling sites

The quality of reservoir feed water and the future potential pressures on the newly shaped reservoir were evaluated by time and spatial variation analysis of Aliakmon River water quality data. For this purpose, existing database for Aliakmon River water quality from 1980-1997 (Ministry of Agriculture, 1998) at two sampling sites that are representative of reservoirs feed water quality were used. "Gefyra Grevenon" sampling site is on the main stream of Aliakmon River. It is representative of the water running from the upper and larger part of the Aliakmon River catchment area (4050 km^2). "Moni Ilarion" sampling site (dam location) is representative of the whole reservoir catchment area, including reservoirs smaller tributaries (catchment area of 662.25 km^2). Available quality data for the years 2007 and 2010 at these sampling sites and measurements taken during the present study in 2012-2013-2014 were also used. Initially, the normal distribution of the data was checked (Sapiro-Wilk method, $p<0.05$, 95% CI), extreme values were estimated (Turkeys method) and were evaluated as isolated cases. An effort to normalize the data did not have satisfactory results and non parametric methods were chosen for further statistical analysis:

a) Time variations of Aliakmon River's physicochemical parameters from 1980 to 2010 were estimated, at the sampling site of "Moni Ilarion". The monthly mean values, from 1980-1997 database (Ministry of Agriculture, 1998), were compared to the limiting values set from the Directives 2006/44/EC for the "quality of fresh water needing protection or improvement in order to maintain fish life" and 79/869/EEC for "surface water intended for drinking water ". To recognize the changes of the feeding water quality over time, a time-series analysis and trend evaluation of water quality parameters for the period 1980-1997, at monthly intervals (Ministry of Agriculture, 1998), as well as individual values for the years 2007 (HCMR, 2009), 2010 (Mergou, 2011) and the measurements taken during the present study (2012-2014) were used.

b) Spatial variation (Mann – Whitney U-test $p<0.05$, 95% CI) of the water quality between the sampling sites of "Gefira Grevenon" and "Moni Ilarion" at monthly interval from 1980 to 2010 was estimated in order to identify the possibility of transported pollution in Ilarion Reservoir from Aliakmon River's basins.

The basic pollution sources of the reservoir aquatic system were identified by correlating the different water quality parameters for the 1980-1997 period by Spearmann correlation method. To assess the spatial and time variations of the reservoir water quality during 2012-2014 and consequently the maturation of the reservoir, the following tests were conducted (Kruskal – Wallis test $p<0.05$, 95% CI and Mann – Whitney U-test $p<0.05$, 95% CI):

a) Spatial and time variations of water quality parameters at the sampling sites during the study period. By this variation the significant statistical differences among the different sampling sites and flooding periods were determined.

b) Spatial and time variation of water quality parameters for the sampling site "Moni Ilarion", between the studied period and the decades 1980-1989 and 1990-1999. By this variation, alterations of water quality due to the initial flooding stage and the formation stages were examined.

3. Results and discussion

3.1. Spatial and time variations of reservoir feed water quality

3.1.1. Extreme values

No extreme values were detected (or less than 5% of total amount of measurements) in the monthly mean values of DO (Fig. 3a), conductivity (Fig. 3b), temperature (Fig. 3c), nitrate nitrogen (Fig. 3d), phosphorus (Fig. 3e) and alkalinity (Fig. 3f), as well as no values over the limits set by Directive 79/869 / EEC (Limits of potable) were observed.

Statistically extreme values were observed for 5% of all pH measurements (Fig. 4a), from which only one marginally exceeded the set limit value for the production of drinking water, but none of them exceeded the critical values for the subsistence of fishes. For the parameter of nitrite nitrogen all statistically extreme values (5.7% of the total measurements) exceeded the maximum permissible limits of Directives concerning fish life preservation (Fig 4b). Also, the extreme values of ammonium nitrogen parameter (13% of the total) exceeded the maximum permissible limit values set for the preservation of salmonids and the production of drinking water (Fig. 4c).

Based on meteorological data, water origin and flow, the extreme values of nitrite nitrogen are mainly linked to the supply from Aliakmon River main flow, where also high concentrations of this parameter are recorded, without excluding the possibility of non point accidental pollution sources.

3.1.2. Temporal variations

Time-series analysis of Aliakmon River water quality for 17 years (1980-1997) with monthly interval and from individual measurements until 2014 (n=6), showed that the majority of parameters had no significant temporal variations (except the parameter of pH) and therefore feed water quality is relatively stable over time (Fig. 5).

3.1.3. Spatial variations

Statistical significant variations between two sampling points were detected, for the parameters of conductivity (Man-Whitney U-test: $p<0.05$), alkalinity (Man-Whitney U-test: $p <0.01$) and nitrate nitrogen (Man-Whitney U-test: $p<0.05$), having higher values of conductivity and alkalinity at sampling site "Moni Ilarion" and nitrate nitrogen at "Gefira Grevenon". The observed increase of conductivity and alkalinity at "Moni Ilarion" can be attributed to the incoming water from Venetikos River and its high alkalinity due to specific geological formations. The high concentrations of nitrate nitrogen observed at "Gefira Grevenon", in the main flow of Aliakmon River, are probably due to fertilizers used for agriculture in that basin.

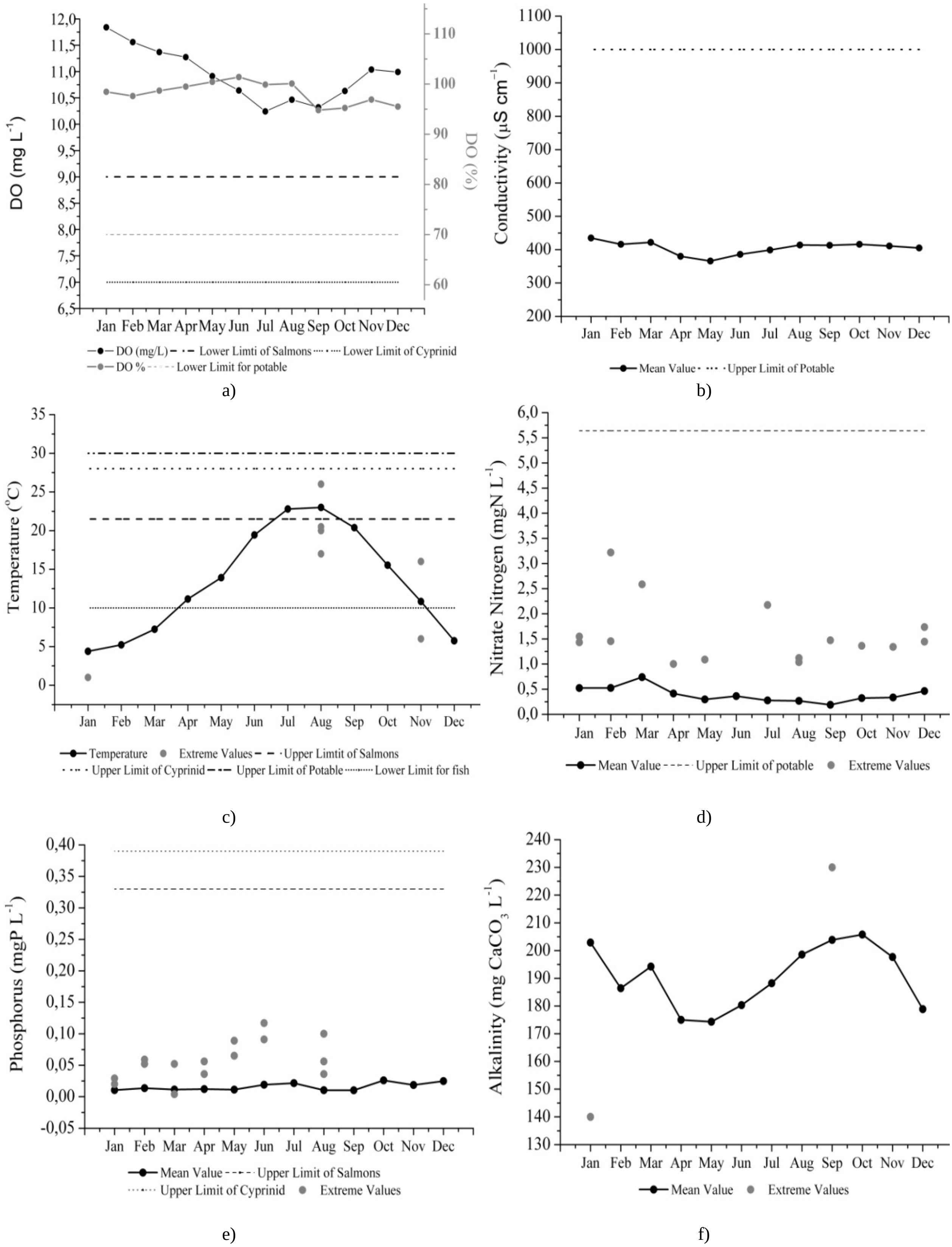
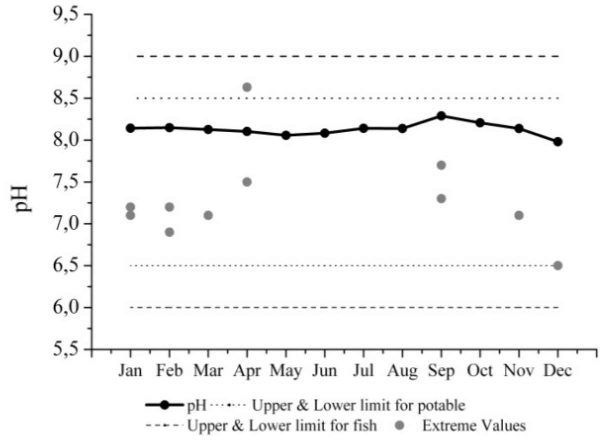
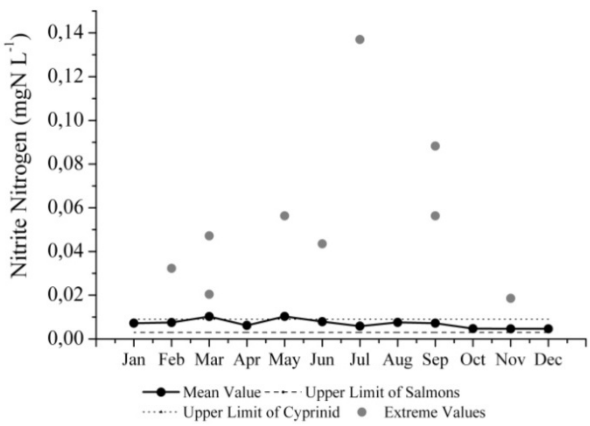


Fig. 3. Monthly interval mean values of Aliakmon River physico-chemical parameters from 1980 to 1997: a) DO%, b) conductivity, c) temperature, d) nitrate nitrogen, e) phosphorus, f) alkalinity



a)



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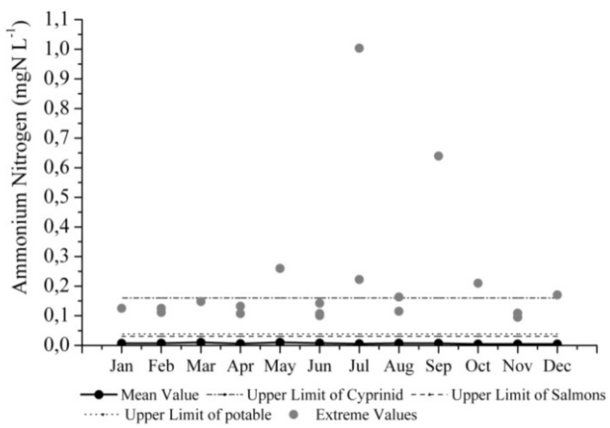
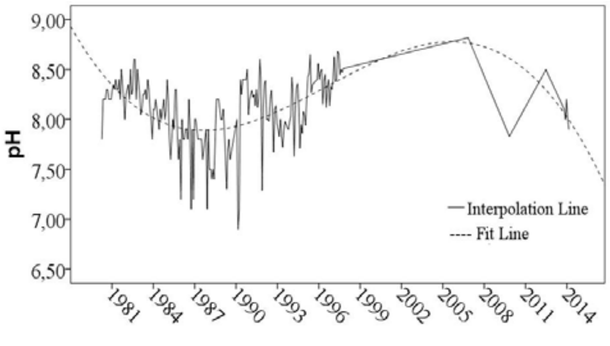
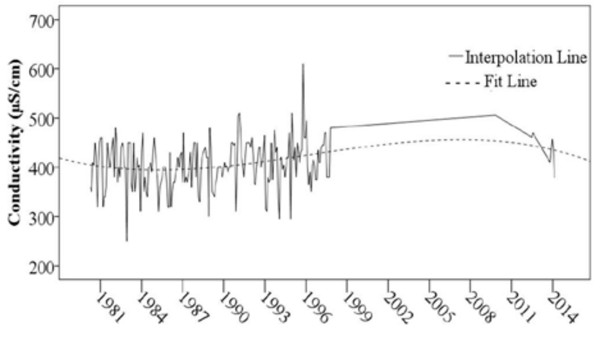


c)

Fig. 4. Monthly interval mean values of Aliakmon River physico-chemical parameters from 1980 to 1997: a) pH, b) nitrite nitrogen, c) ammonium nitrogen



a)



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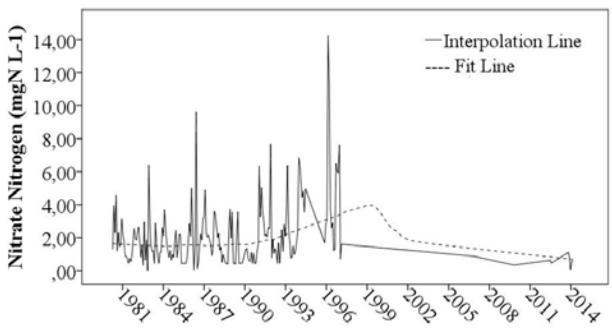

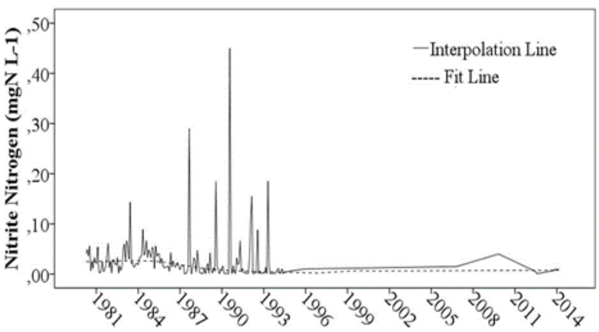

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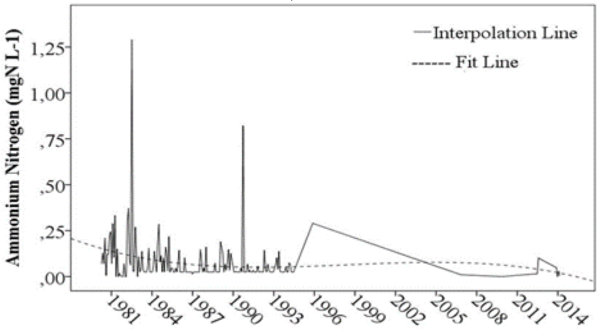
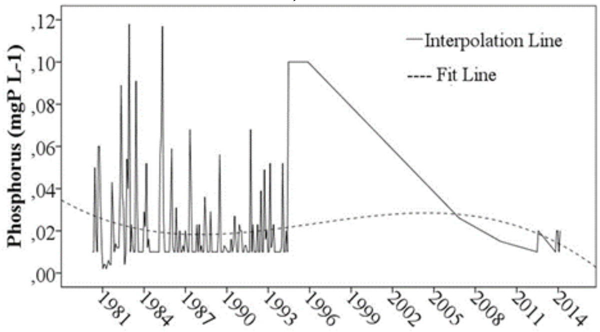


d)



e)

f)

Fig. 5. Temporal variation of Ilarion Reservoir feeding water for the parameters: a) pH, b) conductivity, c) nitrate nitrogen, d) nitrite nitrogen, e) ammonium nitrogen, f) phosphorus

3.1.4. Basic pollution sources

Regarding the source of pollutants, the negative correlation between temperature and nitrate nitrogen ($r = -0.357$, $p<0.01$, $n = 180$), suggests seasonal changes of nitrate nitrogen concentrations. This means that during summer months (high temperature) when flow is low, there is a reduction of nitrate nitrogen, while in winter (low temperatures) when flow increases there is an increase of nitrate nitrogen concentration. The positive correlation between total phosphorus and nitrate nitrogen ($r = 0.273$, $p <0.01$, $n = 168$) suggests that these two parameters might have the same source. The combination of these two parameters is found mainly in fertilizers, but also in urban and livestock wastes. If nitrate nitrogen and total phosphorus were mainly from urban wastes or industrial wastes then one would expect to find at least a correlation of ammonium nitrogen (the non oxidized form of nitrogen) with total phosphorus, which is not observed in our case. Moreover, the non-correlation between nitrate nitrogen and ammonium nitrogen as well as between nitrate nitrogen and nitrite nitrogen reveals that nitrate nitrogen was not formed by oxidation processes and that the different forms of nitrogen do not have the same source. Consequently, considering all the above we are led to the conjunction that fertilizers washed out in river through surface runoff are the most possible source of nitrate and phosphate pollution.

The positive correlation between ammonium nitrogen and nitrite nitrogen ($r = 0.229$, $p<0.01$, $n = 164$) would be expected, as the oxidation of ammonium nitrogen to nitrite nitrogen is a rapid process. Nitrogen compound in its reduced form (ammonia) is oxidized to nitrite in presence of oxygen, causing oxygen deficiency and toxic conditions for aquatic life. The presence of ammonium and nitrite nitrogen shows relatively recent pollution and their source is from municipal and livestock wastewater. From observations in the study area, a large number of scattered animal farms were located around and very close to the reservoir. Microbiological tests in these areas showed that the levels of bacteria exceeded the legislation limit concerning the swimming water usage (Total Coliforms > 1000 Cfu), advocating the conclusion that the pollution source is from livestock activities. The negative correlation between nitrite nitrogen and dissolved oxygen ($r = 0.230$, $p<0.01$, $n = 164$) was also expected, since oxygen is consumed when nitrite nitrogen converts to nitrate.

The positive correlation of alkalinity with conductivity ($r = 0.636$, $p<0.01$, $n = 200$), seems to indicate that the increase in alkalinity is possibly due to high carbonates and bicarbonate ions presence in Venetikos River water, because of the existing limestone in its river basin, as also due to quarrying activities in the area.

Summarizing, the physicochemical characteristics, of Aliakmon River water quality parameters and therefore the quality of the water supplying the newly formed reservoir, is generally within the legislation's limits with the exception of nitrite and ammonium nitrogen which exceed the maximum permissible legislation limits and therefore are considered as the main pollution sources of the new reservoir water quality.

3.2. Spatial and time variations of Ilarion Reservoir water quality during the studying period.

3.2.1. Legislation over limits

No deviations from the limits of the European Directives were observed for the parameters of pH, conductivity, COD and nitrate nitrogen. The other parameters had isolated over limits from the relevant directives at specific sampling sites or periods of sampling.

The TKN values (25% of the total values) were higher than the upper limit of potable water (3 mgN L^{-1}) at sampling sites "Elati" and "Moni Ilarion" from 25/11/2012 to 17/12/2012 and at "Elati", "Moni Ilarion" and "Exit" from 27/04/2014 to 26/05/2014 (Fig. 6a). Decomposition of biomass in the flooded area might be the main source of this organic form of pollution because of the increased concentrations of TKN immediately after the reservoir construction.

Ammonia nitrogen had many measurements (35% of the total values) over the 0.031 mgN L^{-1} upper limit of Salmons preservation and only one over the upper legislation limit of 0.16 mgN L^{-1} Cyprinid preservation at “Elati” sampling site on 17/12/2012 (Fig. 6b).

Furthermore, the concentrations of nitrite nitrogen at “Moni Ilarion” sampling site for the period 03/10/2012 - 24/10/2012 and “Elati” for the period 25/11/2012-17/12/2012 were over the directive limit of 0.009 $mgNO_2$-N L^{-1} (Upper limit for Cyprinid) but have stabilized at lower concentrations since 10/12/2013, the second year of formation (Fig. 6c). During the study period nitrite nitrogen had 15% values over the upper legislation limit for Cyprinid preservation.

Higher values of turbidity (Fig. 6d) were observed (90% of the period total values) during the period of the large flooding (after 25 /11/2012) and exceeded the 4 NTU legislation limit while the concentration of the suspended solids (Fig. 6e) was low during this study period and below the 25 mg L^{-1} legislation limit. At the second year of flooding only isolated incidents of high turbidity occurred mostly at “Karpero” and “Elati” sampling sites (25% of the period total values), and were attributed to weather conditions (wind speed and direction). The increased turbidity at the “Exit” sampling site of the reservoir was temporary and caused from the water turbulent flow at the pipe outlet that ensures the minimum downstream ecological flow from the unformed river bed. At the second year of flooding the necessary infrastructures were completed and no excess turbidity measurements were observed.

The color values were low and below the legislation limit of 10 Hz (Fig. 6f) at all sampling sites until 25/11/2012 (flooding initiation and reservoir creation). After the flooding initiation, an increase of color values was observed, exceeding the legislation limit (30% of the period total values). The higher value was measured at “Karpero” sampling site on 17/12/2012. The high values of color maintained during the second year of the flooding and ranged around the legislation limit of 10 Hz without significant fluctuations. It is obvious that the sudden increase of color values was caused from the dissolution of organic compounds (chlorophyll, colorings etc.).

Summarizing the parameters exceeding the legislation limit in the reservoir during the study period are TKN, ammonia nitrogen, turbidity and color. Time variation of these specific parameters before, during and after reservoir formation will give necessary information for interpreting the exceedances.

3.2.2. Temporal variations

All analyzed water quality parameters at sampling site “Moni Ilarion” for the studied period (2012-2014) had statistically significant differences compared to those of 1980-1997 period for the same months, except of temperature and pH. Significant increased values in 2012 -2014 were found in conductivity (Kruskal-Wallis ANOVA: $H=29.35$, $df=2$, $p<0.01$), alkalinity (Kruskal-Wallis ANOVA: $H= 47.96$, $df=2$, $p<0.01$), ammonium nitrogen (Kruskal-Wallis ANOVA: $H=10.65$, $df=2$, $p<0.01$) and nitrite nitrogen (Kruskal-Wallis ANOVA: $H=34.23$, $df=2$, $p<0.001$). Significant lower values in 2012 were found in dissolved oxygen (Kruskal-Wallis ANOVA: $H=64.255$, $df=2$, $p<0.001$) and nitrite nitrogen (Kruskal-Wallis ANOVA: $H=39.74$, $df=2$, $p<0.001$).

The organic compound dissolution, hydrolysis and corresponding chemical transformation of the submerged plant biomass leads to rapid depletion of dissolved oxygen and release of nutrients in the water body (Bonanomi et al., 2014; Richard et al., 1997; Straskraba et al., 1993; van Der Heide, 1998). In addition more nutrients and elements (P, Mg, Ca, etc) are released from the existing sediments due to anaerobic zones created by low dissolved oxygen concentrations and high depth (Wetzel, 2001). The hydrolysis of carbon substrate under anaerobic conditions leads to acidogenesis and to pH decrease. Decomposition of terrestrial vegetation can last from a few months to several years, depending on the amount and quality of the plant substrate (McClaugherty, 2008). Changes on the water quality will continue until a mature stage of reservoir is achieved.

Between the two different sampling periods of the reservoir formation 2012 and 2013-2014 significant statistical differences also have been noticed for the parameters of pH (Fig 7a) (Mann-Whitney U-test: $p<0.01$), conductivity (Fig. 7b) (Mann-Whitney U-test: $p<0.01$) and turbidity (Mann-Whitney U-test: $p<0.01$) (Fig. 6d). pH values after the reservoir construction tend to decrease at all sampling sites. Conductivity was also more stable at the second year of formation than it was during the first year (smaller deviations were noticed). Turbidity seems to have become stable after the first year of formation but it is highly depended on weather conditions, especially wind.

3.2.3. Spatial variations

No significant spatial variations were observed at the majority of the tested parameters, except those of DO, nitrite nitrogen, color and nitrate nitrogen.

DO concentrations at “Karpero” and “Exit” sampling sites were statistically higher (Fig. 8a) in comparison to the other sampling sites (Mann-Whitney U-test: $p<0.05$), throughout the studying period. The differences in DO concentration at these specific sites were due to their location. “Karpero” sampling site is the nearest to the main tributary of the reservoir and is enriched with dissolved oxygen from it, while “Exit” site is actually a river with high turbulence. It is worth mentioning the decrease of DO saturation levels at sampling site “Elati” (Fig. 8b) started from 07/11/2012, the period when site flooded and formed a pond lake.

The parameter of nitrite nitrogen at sampling site “Exit”, (Fig. 4c), downstream the dam, had statistically lower values in comparison to the other sampling sites during the whole study period (Mann-Whitney U-test: $p<0.01$) due to the rapid ammonia nitrogen oxidation produced from the organic compounds hydrolysis after flooding. On the other hand, nitrate nitrogen at sampling site "Exit" (downstream the dam) (Fig. 8c) had higher values in comparison to "Moni Ilarion" site (Mann-Whitney U-test: $p<0.01$) especially during 03/10/2012 to 07/11/2012 period (flooding period), due to rapid oxidation of nitrites to nitrates. The color values (Fig. 4f) were statistically higher at sampling site "Karpero" than the other sites. The shallow water of the reservoir at this location, around 20 m, as compared to a maximum of 85 m, combined with the flooded vegetation of the area may justify this observation. Consequently, the whole aqueous system of Ilarion young reservoir after two years of formation has high levels of dissolved oxygen concentrations and does not seem to have reached its stabilization age but a stabilization tendency appears in the concentrations of TSS, conductivity and nitrate nitrogen. Changes in the volume of the water and the gradual flood of areas covered with plant residues, affected the water quality with significant spatial variations, while excesses of the legislation's limits for some parameters were frequently observed.

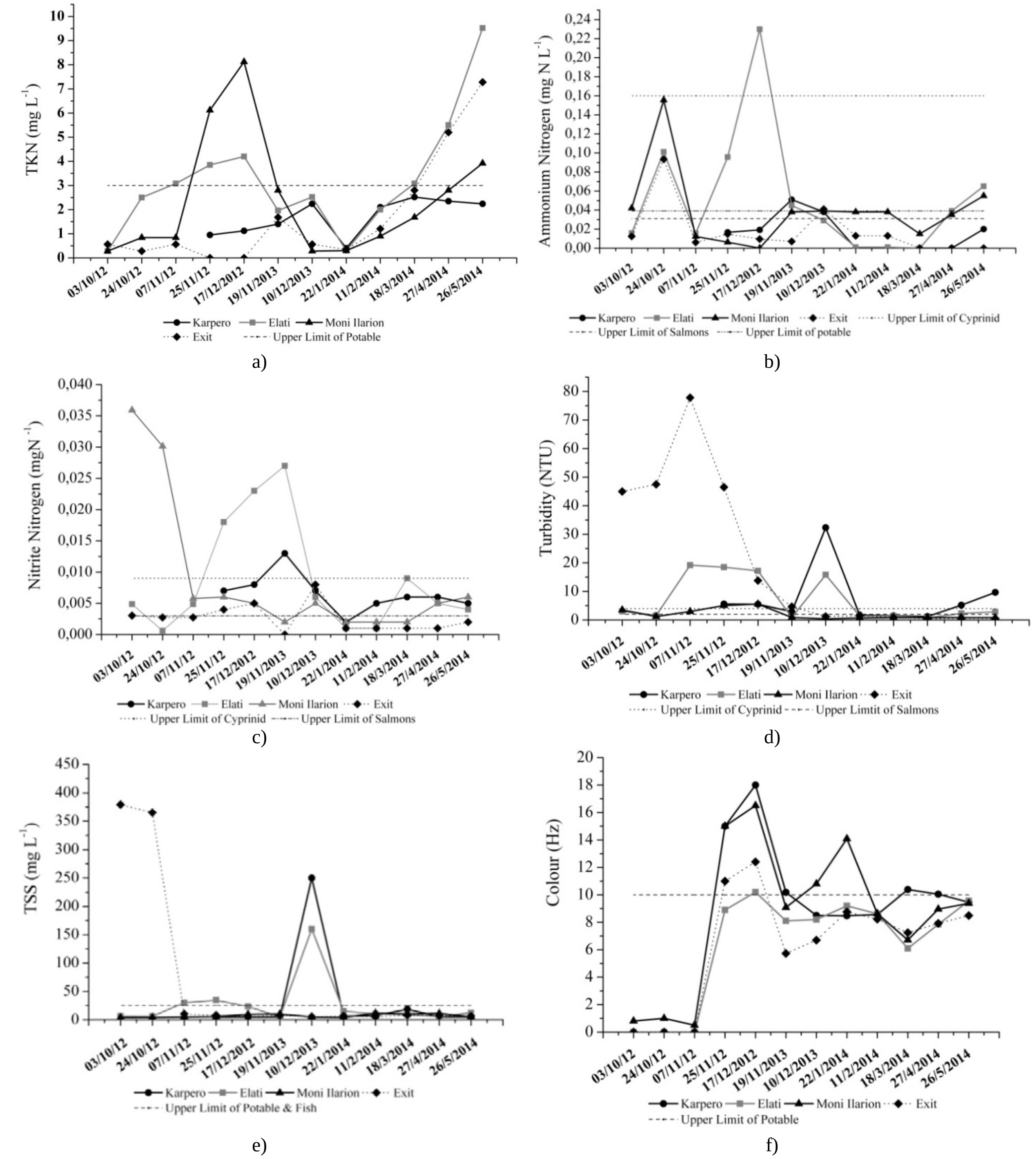


Fig. 6. Spatial and time variation of the following parameters at Reservoir Ilarion sampling sites for the study period (2012-2014): a) TKN, b) ammonium nitrogen, c) nitrite nitrogen, d) Turbidity e) TSS and f) color

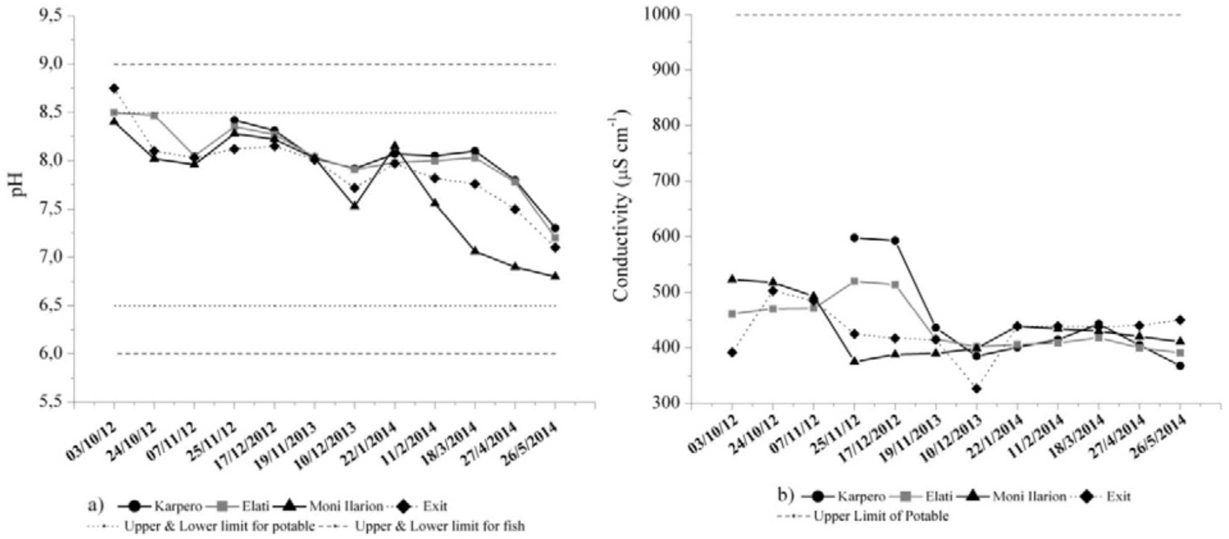


Fig. 7. Spatial and time variation of the following parameters at Reservoir Ilarion sampling sites for the study period (2012-2014): a) pH, b) conductivity

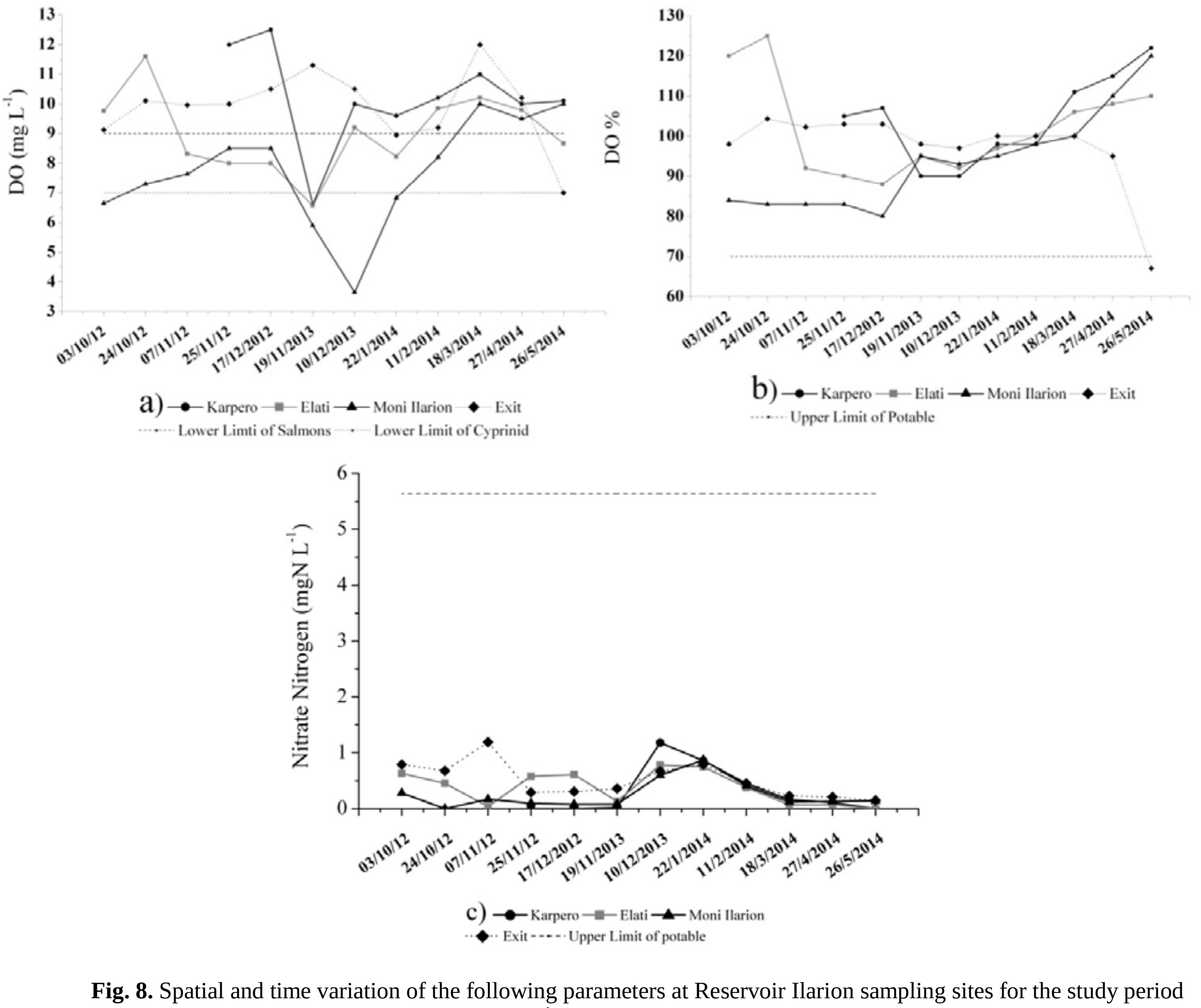


Fig. 8. Spatial and time variation of the following parameters at Reservoir Ilarion sampling sites for the study period (2012-2014): a) Dissolved Oxygen (mg L^{-1}), Dissolved Oxygen Saturation %, d) nitrate nitrogen

4. Conclusions

Water quality monitoring and data statistical interpretation are helpful tools to estimate pollution sources and ecological status for efficient management of water resources. Spatial and temporal statistical analysis on the young reservoir feeding water quality data has shown excesses of legislation's limits for ammonia and nitrite nitrogen. Their source is possibly from municipal and livestock wastewater. In flooded area, legislation exceedings for TKN, ammonia nitrogen, nitrite and color were observed due to biomass decomposition in the flooded area. These parameters are the main future pollutants and their monitoring is necessary, because they lead to eutrophication and toxic conditions for fishes.

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