A Comparative Study of Water Quality and Trophic State Contribution on Natural and Artificial Lakes Global Warming Potential

Georgios Samiotis
University of Western Macedonia
Charoula Mavromatidou
University of Western Macedonia
Maria Ziagova
University of Western Macedonia
Eleni Trikilidou
University of Western Macedonia
Elisavet Amanatidou (eamanatidou@uowm.gr)
University of Western Macedonia

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A comparative study of water quality and trophic state contribution on natural and artificial lakes global warming potential

Georgios Samiotis[1], Charoula Mavromatidou[1], Maria Ziagova[1], Eleni Trikilidou[1], Elisavet Amanatidou[1*]

[1]Laboratory of Environmental Chemistry & Water and Wastewater Treatment, Department of Chemical Engineering, University of Western Macedonia, Kozani, Greece

*Corresponding author, email: eamanatidou@uowm.gr

Abstract

Natural lakes and reservoirs are emitters of GHGs in the atmosphere contributing to 31% of the annual CO_2 emissions of those from fossil fuel combustion. Measurements of GHGs emissions in reservoirs demonstrate that hydropower may actually not be as “green” as once thought. It is estimated that emissions from reservoirs may be equivalent to 7% of the global warming potential (GWP) of other documented anthropogenic emissions. Aim of this work is to assess the impact of water quality deterioration and the subsequent increment of biological productivity of a waterbody on GHGs emissions. Therefore, the trophic state, the carbonic GHGs emissions and the GWP of one natural lake domestic wastewater receiver and two different age hydroelectric reservoirs, located in North West Greece, were studied. Gross emissions of CO_2 and CH_4 were in-situ measured using a static floating chamber and specific emissions as well as GWP were calculated. Furthermore, water quality and trophic state were evaluated based on the application of ΥΔΩΡ (hydõr) Water Quality Index and Florida Trophic State Index using physicochemical characteristics measurements. Data statistical interpretation revealed that CH_4 has strong positive correlation with GWP, temperature, water quality and trophic state. There is a seasonal variation of GWP that follows the seasonal variation of CH_4 emissions induced by water temperature. Specific CH_4 emission rate presents the most reliable indicator for assessing the impact of a waterbody in terms of GWP, especially of a hypertrophic one. Water quality and trophic state indices can be used for a rough comparison of GWP between waterbodies with the same climatic conditions.

Keywords: Global warming potential, GHGs emissions; waterbodies, water quality, water quality index, trophic state index.

1. Introduction

Anthropogenic activities, such as fossil fuel combustion, livestock, deforestation and creation of artificial wetlands significantly increase the concentration of greenhouse gases (GHGs) in the atmosphere and enhance greenhouse effect [1,2]. Natural lakes, freshwater reservoirs and other surface waters are of particular interest, since lentic ecosystems emit 110-810 Tg CO_2-C and 69–112 Tg CH_4-C annually, constituting a great subject of discuss in the heart of a worldwide debate [2,3,4]. Their contribution on annual CO_2 emissions is estimated at approximately 31% of those from fossil fuel combustion [5]. Measurements of GHGs emissions in reservoirs demonstrate that hydropower may actually not be as “green” as once thought. It is estimated that emissions from reservoirs may be equivalent to 7% of the global warming potential (GWP) of other documented anthropogenic emissions [6].

GHGs emissions from aquatic systems are highly influenced by waterbody's trophic state, which in turn is a function of nutrients availability, usually phosphorous and less often nitrogen, as well as other parameters such as seasonal variations, grazing of phytoplankton by zooplankton, mixing depth of water, etc. [7-11]. According to European Environment Agency [12] the trophic status of a waterbody is classified into 5 categories, Oligotrophic, Oligo/Mesotrophic, Mesotrophic, Meso/Eutrophic and Eutrophic. The term Hypereutrophic has been also used for characterizing highly eutrophic waterbodies including artificial lakes mainly the first years of their formation [13,14].

In freshwater reservoirs, carbon dioxide and methane are formed due to organic matter imported from the catchment area or produced due to plants and soils decomposition [14]. More specifically, CO_2 is produced mainly in oxic (aerobic) conditions and sometimes in anoxic conditions in the water column, impounded soils and sediments of the reservoir, whereas is consumed (carbon fixation) by aquatic primary producers in the euphotic zone of a reservoir [15, 16]. GHGs emissions are highly influenced by organic carbon in soils and topography. Reservoirs that flood peatlands emit more greenhouse gases in the long term than reservoirs built in canyons where little area is flooded, with limited peat deposits [6].

In general, carbon dioxide emissions increase from oligotrophic to eutrophic lakes. Methane is produced under anaerobic conditions, primarily in the sediments, a portion of which is oxidized to CO_2 by methanotrophic bacteria in both water column and sediments [17]. The fraction of CH_4, which is oxidized before being emitted to the atmosphere, varies across freshwater aquatic systems depending on oxygen levels and temperature [18].

Since nutrient availability is directly related to organic matter decomposition, monitoring and assessing the trophic state (status) of an aquatic system is essential to evaluate the environmental impact of reservoirs. The trophic status of an aquatic system indicates its environmental health and is expressed by a basic classification scale showing rather its biological productivity than its water quality. Trophic status can be calculated using Trophic State Indices (TSI), combining quality parameters, usually water clarity, algal activity, phosphorus and nitrogen availability [19].

On the other hand, water quality assessment of an aquatic system is a more complicated procedure due to the numerous physicochemical and biological parameters that may affect it [20]. The plethora of factors needed to yield a single result of the overall water quality, such as (i) the large number of data necessary for the qualitative evaluation, (ii) the special knowledge and expertise required, as well as the (iii) difficulties arising in combining qualitative parameters characterized by different significance and expressed in different units of measurement and concentration ranges, make the assessment process particularly difficult [21]. A widely applied methodology for conveying the different water quality parameters in one single expression is the calculation of a Water Quality Index (WQI). A WQI is a number, a scale, a word, a symbol or a color that expresses the water quality of an aquatic system at a specific area in a specific period [22, 23].

According to literature review, there are limited data regarding the correlation of a waterbody's water quality and trophic state with GHGs emissions and subsequently GWP. Aim of this work is to correlate water quality and trophic state indices as well as GHGs emissions with GWP in order to obtain indicators for easily assessing GWP of waterbodies. For this purpose, one natural lake and two hydroelectric reservoirs were studied. Physicochemical characteristics and gross emissions of CO_2 and CH_4 were measured. Water quality and trophic state indices, as well as specific emissions and GWP were calculated and statistically interpreted.

2. Materials and methods

The research methodology of this work includes the selection of sampling stations and the measurement of water physicochemical parameters, CO_2 and CH_4 emissions in the collected samples. Thereafter, calculation of specific emission rates and GWP was carried out, whereas water quality and trophic state indices were also calculated. The obtained data were statistically processed using SPSS software and interpreted accordingly.

2.1. Study area

A natural lake (Zazari Lake) and two hydroelectric reservoirs (Ilarion and Polyfytos Reservoirs) were selected for the comparative assessment of GHGs emissions, water quality and trophic state. All three waterbodies are located in the area of North-West Greece presenting the same climatic conditions. (Figure 1).

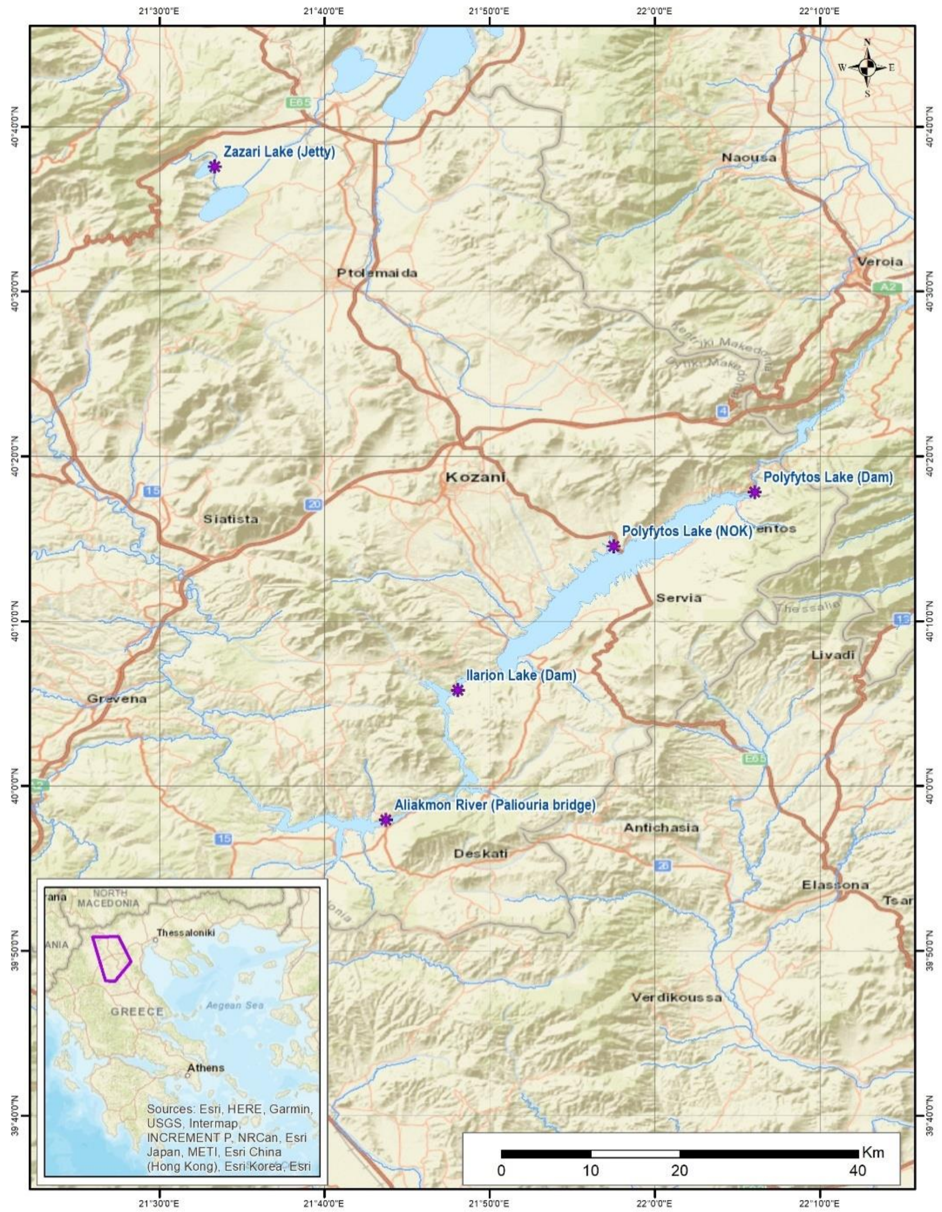

Figure 1. Study area map and sampling stations.

Zazari Lake is located in a relatively small flat area approximately 60 km North-West of Ilarion and Polyfytos Reservoirs, covering a surface of approximately 1.7 km^2, with a maximum depth of approximately 6 m and is used mainly for irrigation and fishing. Five years ago, Zazari Lake was the final receiver of domestic wastewater from neighboring villages.

Ilarion and Polyfytos Reservoirs were created in 2012 and 1975 respectively, for the production of hydroelectric energy. Both reservoirs are fed with water from Aliakmon River, which is the longest river in Greece (approximately 300 km).

Ilarion Reservoir is a relatively young and small reservoir downstream Aliakmon River, created in stiff rocky hills, forming a deeper canyon-like lake (terrain slopes between 15° to 45°). It covers a total surface of 22 km^2 with a maximum depth of 65 m. Prior to its impoundment, 23.1% was river, 53.03% was non-forest soil (grassland, rocks, and agricultural land), and 23.96% was forest (plane and oak trees) [24]. Limited agricultural and livestock activities and absence of other anthropogenic pressures characterize the area.

Polyfytos Reservoir is significantly older and larger than Ilarion, having a surface of 73 km^2 with a maximum measured depth of 22 m. It was created in a rather flat agricultural area where Neraida village was located. Agricultural and livestock activities characterize the area around the reservoir prior and post their impoundment [24, 25].

2.2. Sampling and measurements

Five sampling stations were selected (Figure 1), one in Zazari Lake, two in Polyfytos Reservoir, one in Ilarion Reservoir and one in Aliakmon River (sampling station Paliouria Bridge, western end of Ilarion Reservoir). The maximum measured depth of the sampling stations varied from 4.5 m to 6 m for Zazari Lake, 12 m to 14 m for Polyfytos NOK, 10 m to 12 m for Polyfytos Dam and 5 m to 7 m for Ilarion Dam. The measured depth of Aliakmonas River at the sampling station Paliouria Bridge ranged from 0.3 m to 1 m. All samplings were carried out from January 2018 to February 2019; samples were collected from surface (0.3 m) and maximum depth in every sampling station. Table 1 summarizes all the necessary details of the sampling plan performed in North-West Greece.

Table 1. Sampling stations, sampling points, number of samples and type of performed measurements.

Sampling station	Sampling point	Number of samples	Type of Measurements
Ilarion Reservoir	Ilarion Dam	10	Physicochemical measurements in water and in situ gross CO_2 and CH_4 emission measurements
Polyfytos Reservoir	Polyfytos Dam	10	Physicochemical measurements in water and in situ gross CO_2 and CH_4 emission measurements
	Nautical Club of Kozani (Polyfytos NOK)	10	
Zazari Lake	Jetty (South-West coast)	8	Physicochemical measurements in water and in situ gross CO_2 and CH_4 emission measurements
Paliouria Bridge	Aliakmon River	6	Physicochemical measurements in water

A sub-surface water sampler was used for the collection of water samples. Water temperature and dissolved oxygen were measured in situ with a properly calibrated optical dissolved oxygen meter (Hach HQ30d).

All water samples were analyzed within a few hours from sampling by the accredited, according to ISO 17025, Environmental Chemistry & Water and Wastewater Treatment Laboratory, of the University of Western Macedonia, Greece. The parameters of pH, Conductivity, Color, Turbidity, Ammonium ions (NH_4^+), Nitrite ions (NO_2^-), Total suspended solids (TSS), Hexavalent Chromium (Cr^{+6}), Total organic Carbon (TOC), Total Kjeldahl Nitrogen (TKN), Total Phosphorus (TP), Hardness, Alkalinity and Chlorophyll-α were analyzed according to standard methods [26]. The parameters of Cl^-, NO_3^-, SO_4^{-2}, K^+, Na^+, Ca^{+2} and Mg^{+2} were analyzed by Ion

Chromatography (IC), according to ISO 10304-1 (2007) and ISO14911 (1998) [27, 28], using a Metrohm Chromatographer (model 881 Compact IC pro), equipped with an electrical conductivity detector and two Metrosep columns (models A SUPP 5 250 and C 2 250/4).

For the collection of GHGs emissions, specifically CO_2 and CH_4, a static floating chamber was used. The static floating chamber was a close-ended, stainless steel, rectangular box, 0.50 m in height, 0.50 m in width, and 1 m in length, equipped with a floating buoy, constructed using a 0.20 m Ø rubber tube, filled with polyurethane foam. Gas samples were collected after 0 min, 50 min, 90 min, 130 min, and 180 min in low permeability, multi-layered foil bags (Supel™ - Inert Multi-Layer Foil Bag), suitable for gas sample collection. Gas chromatography for the determination of CO_2 and CH_4 concentrations was performed using a SHIMADZU 14B, equipped with thermal conductivity (TCD) and flame ionization (FID) detectors as well as with a Molecular Sieve 13× (10 ft. × 1/8 in.) and a Porapack QS (10 ft. × 1/8 in.) column for gas separation. Both columns were heated at 80°C.

The specific GHGs emission rate was calculated according to Equation (1), using CO_2 and CH_4 concentration measurements with the static floating chamber previously described.

$$C = \rho \times \frac{dC}{dt} \times \frac{273}{273+T} \times H \qquad (1)$$

where: *C* is the specific gas emission rate (mg m^{-2} h^{-1}); ρ is the gas density in standard conditions (kg m^{-3}); *dC/dt* is the linear regression of gas concentration in static floating chamber; *H* is the height (m) from the chamber top to the water surface; *T* is the air temperature (°C) inside the chamber [29].

2.3. Characterization of water quality

Water quality classification was carried out using a new WQI developed at the department of Chemical Engineering - University of Western Macedonia, named *YΔΩPWQI* (hydõr = water in ancient Greek). *YΔΩPWQI* is considered to be a sensitive and flexible tool for assessing water quality, as it (a) prioritizes monitoring parameters, (b) redefines weight coefficients based on experts' opinion, (c) inserts in its calculation the ideal values, (d) takes into consideration both legislation and experts' opinion and (e) is sensitive to marginal conditions, in contrast to other water quality indices [30, 31]. *YΔΩPWQI* is calculated by Equation 2.

$$Y\Delta\Omega PWQI = \frac{\sum_{i=1}^{n}[Average(q_i \times RWi)] + \sum_{i=1}^{n}\left[Ri,e \times Average\left(q_{i,e} \times RWi\right)\right]}{\sum_{i=1}^{n} RWi} \quad (2)$$

where: *qi* is the Sub-index of sample for *i* parameter; *qi,e* is the Sub-index of sample for *i* parameter exceeding permitted value; *RWi* is the relative weight of *i* parameter (obtained from Mavromatidou et al., 2020)[30]; *Ri,e* is the ratio of samples exceeding permitted value of parameter *i* to total number of samples of parameter *i*; *n* is the number of control parameters

The sub-index is calculated according to Equation (3), which is taking under account the measured physicochemical and microbiological water quality parameter values, the standard values deriving from legislation limits and the desired or ideal values.

$$q_i = \frac{100 \times |C_i - V_{i0}|}{|S_i - V_{i0}|} \quad (3)$$

where: *Ci* is the measured value of the *i* water quality parameter; *Si* is the permitted *i* water quality parameter value obtained from legislation; *Vio* is the ideal value of *i* water quality parameter.

The parameters included in the calculation of *YΔΩPWQI* were: Hexavalent Chromium, *E-coli*, Lead, Arsenic, Cadmium, Fecal Coliforms, Total Pesticides, Mercury, Ammonium, COD, Nitrite Ions, Nitrate Ions, Total Phosphorus (TP) and Chlorides (Total Pesticides, Lead, Arsenic, Cadmium and Mercury measurement data were provided from the Greek Ministry of Rural Development and Food, (2020 a,b)[32, 33]). The permitted values of control parameters were obtained from the limit values of European directives and national legislation regarding quality of internal surface, ground and drinking waters. For ideal values, the Lower Detection Limit (LDL) of each parameter was used. The classification of water quality according to *YΔΩPWQI* is presented in Table 2.

Table 2. Characterization of lakes according to *YΔΩPWQI* results (Mavromatidou et al., 2020).

***YΔΩPWQI* scale**	**Water Quality Characterization** (Based on physicochemical and microbiological characteristics)
0 ≤ *YΔΩPWQI* ≤ 10	Excellent
10 < *YΔΩPWQI* ≤ 25	Good
25 < *YΔΩPWQI* ≤ 50	Fair
50 < *YΔΩPWQI* ≤ 100	Marginal
YΔΩPWQI >100	Poor

2.4. Characterization of trophic state

Trophic state characterization of every waterbody was based on the calculation of a TSI, more specifically, the Florida TSI (*FTSI*) [13, 34]. *FTSI* is based on the same rationale as that of Carlson (1977)[35], who introduced the concept of classifying the trophic state of a waterbody using measurement data regarding Turbidity (Secchi depth), Chlorophyll concentration and TP concentration. *FTSI* excluded turbidity, while included the parameter of Total Nitrogen (TN) as a third indicator. Turbidity was excluded because it was causing problems in dark-water lakes and estuaries, where dark-waters rather than algae diminish transparency [34].

In order to apply *FTSI*, each waterbody's limiting nutrient, must be determined, which is usually phosphorous and less often nitrogen [13]. The limiting nutrient is determined based on the ratio of TN concentration to TP concentration. For TN/TP < 10 the liming nutrient is Nitrogen, for TN/TP > 30 is Phosphorus, while for 10 ≤ TN/TP ≤30 there is no limiting nutrient (nutrient balanced waterbody) [36]. Regarding *FTSI* calculation in Polyfytos reservoir, mean values of TP, TN and Chlorophyll *α* from the two sampling stations were used.

For the determination of the overall trophic state index using *FTSI*, a separate component (sub-index) for each parameter was calculated, depending on the limiting nutrient, using the appropriate formula (Equation 4 to Equation 8), followed by the appropriate combination of the sub-indexes, as indicated in Equation A to Equation C. The equation for the calculation of Chlorophyll *a* sub-index ($CHLA_{TSI}$) is the same (Equation 4) regardless the limiting nutrient. On the contrary, the nutrient status of a lake dictates the empirical formula that is used for Nitrogen and for Phosphorus sub-indices calculation. For nutrient-balanced lakes (10 ≤ TN/TP ≤30) Equation 5 and Equation 6 are used; for phosphorus-limited lakes (TN/TP >30), Equation 7 is used, whereas for nitrogen-limited lakes, Equation 8 is used

FTSI sub-index formulas:

$$CHLA_{TSI} = 16.8 + [14.4 \times ln(CHLA)] \quad (4)$$

$$TP_{TSI} = [18.6 \times ln(TP \times 1000)] - 18.4 \quad (5)$$

$$TN_{TSI} = 56 + [19.8 \times ln(TN)] \quad (6)$$

$$TP2_{TS} = 10 \times [2.36 \times ln(TP \times 1000) - 2.38] \quad (7)$$

$$TN2_{TSI} = 10 \times [5.96 + 2.15 \times ln(TN + 0.0001)] \quad (8)$$

FTSI overall index formulas:

$$TSI = \frac{CHLA_{TSI} + \frac{TN_{TSI} + TP_{TSI}}{2}}{2} \quad (A)$$

$$TSI = \frac{CHLA_{TSI} + TP2_{TSI}}{2} \quad (B)$$

$$TSI = \frac{CHLA_{TSI} + TN2_{TSI}}{2} \quad (C)$$

Based on the results of overall *FTSI*, the waterbodies are classified according to their trophic state as “Oligotrophic”, “Mid-Eutrophic”, “Eutrophic” and “Hypereutrophic” and corresponds to “Good”, “Fair” and “Poor” water quality respectively (Table 3). A "Good" lake water quality is one that meets all lake-use criteria (swimmable, fishable and supports healthy habitat); a “Fair” lake water quality can be considered highly productive and a reasonable lake for fishing and most water sports, while a “Poor” lake water quality means that probably the lake use criteria are not meet [13].

Table 3. Classification and characterization of lakes according to *FTSI* results [13].

***FTSI* scale**	**Trophic State Classification**	**Water Quality Characterization** (Based on trophic status)
0 to 59	Oligotrophic through Mid-Eutrophic	Good
60 to 69	Mid-Eutrophic through Eutrophic	Fair
70 to 100	Hypereutrophic	Poor

2.5. Global Warming Potential Calculation

The Global Warming Potential was developed to allow comparisons of the global warming impacts of different gases. Each greenhouse gas has different GWP. CO_2, by definition, has a GWP of 1 regardless of the time period used, because it is the gas being used as the reference. CH_4 is considered to have 20 times higher GWP than that of CO_2 on over a 100 to 150-year period [37].

The calculation of GWP in relation to season and for a monthly step, was carried out using the average values of CO_2 and CH_4 specific emissions for the year 2018, as well as from 2014 to 2016 as described in our previous work [24].

2.6. Data evaluation and statistical analysis

The samples' analysis results were statistically processed and interpreted using the SPSS statistical software. For testing the significant differences among the values of the measured parameters corresponding to depth and surface samples, the independent variables *t*-test was used. A significance level of 0.05 or 95% confidence interval was set. For the evaluation of correlation between measured and calculated parameters, the Spearman's rank correlation hypothesis test was applied setting a significance level of 0.05.

3. Results and Discussion

3.1. Assessment of significant differences between sampling stations

Independent variable *t*-test between the measured physicochemical parameters of surface and maximum depth samples at all sampling stations (comparative data from the first three samplings) showed that:

- Polyfytos and Ilarion Reservoir presented no significant statistical difference (Sig. > 0.05) for none of the twenty-two examined parameters.

This may be attributed to the low hydraulic residence time due to water discharges as well as the continuous mixing of the waterbody's layers from dam [25, 38].

- In Paliouria Bridge, due to its low depth, no stratification occurred and hence no significant differences in water quality were observed; none of the twenty-two examined parameters presented significant statistical differences between surface and depth samples. Paliouria Bridge sampling station in Aliakmon River is a river to lake transition area that inundated last and has significant changes in depth due to dam operation and Aliakmon River flow [25].
- In Zazari Lake, only chlorophyll *a*, exhibited significant statistical difference between surface and depth samples (*t*-test, Sig.= 0.001). This may be attributed to water stratification of the lake, due to phototrophic organisms' growth. The relatively high turbidity and color in Zazari Lake as well as its relatively low mixing of water, indicative of natural lakes, may cause higher growth rate of phototrophic organisms at the surface of the lake in relation to those present in the deeper levels, where the transfer of photosynthetically active radiation (PAR) is significantly obstructed [5, 39]. Leach et al. (2018) found that the variation in chlorophyll *α* concentrations with depth in lake water is influenced more by light attenuation than thermal stratification [40]. Reservoirs differ from natural lakes in terms of hydraulic residence time (HRT), loads of total suspended solids, and productivity [38, 41]. Moreover, hydrological variability induced by anthropogenic manipulation of inflow/outflow can affect the variation with depth in constituents in lakes and reservoirs.

Due to the non-significant statistical differences between surface and depth regarding the examined parameters in all sampling stations, as well as due to the fact that the differences in chlorophyll *a* measurements between surface and depth in Zazari Lake did not affect either the characterization in terms of water quality and trophic state or the results of statistical correlations, all subsequent water samples were collected only from the maximum depth.

Independent variable *t*-test between the measurements of physicochemical parameters at the two sampling stations of Polyfytos Reservoir (Figure 1, Polyfytos Dam and Polyfytos NOK) showed that there are non-significant differences (Sig > 0.05) regarding 20 of the 22 examined parameters. According to the results of the statistical analysis only nitrates and turbidity presented significant statistical differences (Sig. = 0.002 and 0.029 respectively). Nevertheless, these differences in nitrates and turbidity measurements between the two sampling stations of Polyfytos Reservoir did not affect either the characterization in terms of water quality and trophic state or the results of statistical correlations. Thus, both Polyfytos sampling stations were accounted as one for the calculation of *YΔΩPWQI* and *FTSI*, as well as for the statistical analysis between all sampling stations.

In Table 4, the average values of each physicochemical parameter in every sampling period along with their standard deviation are presented.

Table 4. Average values and standard deviation of physicochemical parameters at maximum depth of each sampling station

Parameter	Zazari Lake	Std. Dev.	Ilarion Reservoir	Std. Dev.	Polyfytos Reservoir	Std. Dev.	Paliouria Bridge	Std. Dev.
pH	8.17	0.61	8.13	0.31	8.17	0.34	8.22	0.18
D.O., % saturation	118	6.20	82	10.41	102	20.67	100	15.34

Conductivity, μS/cm	175.66	11.37	388.25	20.89	405.17	29.83	402.05	56.57
Color, Hazen	8.62	5.08	10.34	4.46	6.99	3.72	24.05	9.12
Turbidity, NTU	5.51	8.70	1.77	1.04	1.18	1.42	75.30	57.70
TSS, mg/l	11.60	1.27	2.63	1.80	3.1	1.87	22.20	17.07
NO_3^-, mg/l	0.53	0.39	1.18	0.99	1.11	0.86	1.90	0.78
NO_2^-, μg/l	7.32	5.73	23.78	14.36	12.48	11.31	52.75	21.05
NH_4^+, mg/l	0.11	0.21	0.11	0.22	0.02	0.03	0.03	0.03
Alkalinity, mg/l	92.96	80.44	179.16	15.66	205.60	20.53	204.20	23.05
Hardness, mg/l	63.21	15.06	213.75	21.05	216.95	65.50	148.80	46.67
Cl^-, mg/l	4.09	1.31	5.47	0.88	6.56	2.70	6.40	1.58
TOC, mg/l	4.49	6.34	5.19	3.90	3.73	3.28	5.75	1.34
TKN, mgN/l	4.65	2.62	1.40	0.61	1.78	0.90	1.89	0.30
Ca^{+2}, mg/l	15.60	0.71	34.80	3.41	38.61	5.36	22.75	12.87
Chlorophyll *a*, μg/l	18.89	1.70	1.40	0.76	2.55	1.98	0.52	0.63
Cr^{+6}, μg/l	6.15	1.49	2.43	1.01	0.76	1.40	4.70	7.12
TP, mgP/l	1.29	1.41	0.007	0.004	0.45	0.49	0.083	0.055
Na^+, mg/l	7.98	0.60	5.46	2.08	5.88	1.12	5.81	6.14
K^+, mg/l	3.46	0.25	1.57	0.22	1.65	0.06	1.40	1.28
Mg^{+2}, mg/l	4.45	0.30	25.80	0.35	22.74	1.07	22.20	1.69
SO_4^{-2}, mg/l	8.50	1.20	22.34	5.42	19.16	4.15	18.3	3.34

The high standard deviation values in various parameters of Table 4 are indicative of changes of water quality between samplings. Nevertheless, the high differences in measured values did not hinder the results regarding the characterization of the waterbodies in terms of water quality and trophic state, since the application of *YΔΩPWQI* and *FTSI* using average parameter values plus their standard deviation presented similar results and identified the differences between the three waterbodies.

As it can be seen in Table 4, all sampling stations of Aliakmon River basin except Zazari Lake present similar water quality characteristics. Statistical analysis of all physicochemical parameters between all sampling stations showed significant differences (*t*-test, $p < 0.05$) only in Zazari Lake.

The similar water quality of sampling stations at Aliakmon River basin is attributed to their common feed. More specifically, water of Paliouria Bridge supplies Ilarion Reservoir, which thereafter replenishes Polyfytos Dam. Higher values of Color, Turbidity and TSS were only reported in Paliouria Bridge sampling station, due to the shallow depth (0.3- 1 m) and the flow of Aliakmon River.

3.2. Assessment of water quality, trophic state and carbonic emissions

The waterbodies quality and trophic state classification according to *YΔΩPWQI* and *FTSI* respectively, as well as CO_2 and CH_4 specific emissions are presented in Table 5. *YΔΩPWQI* and *FTSI* were calculated as described in Materials and Methods, sections 2.3. and 2.4., based on the average measured values (Table 4). The range of CO_2 and CH_4 specific emissions as well as the average specific emissions were calculated as described in Materials and Methods, section 2.2., based on measured emission rates using a static floating chamber.

Table 5. Measurement data; classification / characterization of waterbodies based on *FTSI* and *YΔΩPWQI* calculation.

Parameter	**Ilarionas Reservoir**	**Polyfytos Reservoir**	**Zazari Lake**
TN/TP ratio	137	4.07	3.71
Nutrient status	Phosphorus-Limited Lake	Nitrogen-Limited Lake	Nitrogen-Limited Lake
FTSI	20.1	51.4	76.3
FTSI classification	Oligotrophic through Mid-Eutrophic	Oligotrophic through Mid-Eutrophic	Hypereutrophic
FTSI characterization	GOOD	GOOD	POOR

YΔΩPWQI	21.4	45.2	112.5
YΔΩPWQI characterization	GOOD	FAIR	POOR
Specific CO_2 emission rate (mg m^{-2} d^{-1})	65.8 to 1144.8	98.0 to 761.4	-731.9 to 2000.7
Average specific CO_2 emission rate (mg m^{-2} d^{-1})	389.8	391.9	309.7
Specific CH_4 emission rate (mg m^{-2} d^{-1})	0 to 19	0 to 43.2	0 to 2236.9
Average specific CH_4 emission rate (mg m^{-2} d^{-1})	4.6	13.3	673.4

The water quality of the older and considered stabilized Polyfytos Reservoir and the younger Ilarion Reservoir is characterized as “Fair” and “Good” respectively, according to *YΔΩPWQI* (Table 5). On the contrary, in our previous work (2012-2015 monitoring period) and during Ilarion Reservoir maturation period, Polyfytos Reservoir was characterized by better water quality than Ilarion [25]. Taking into consideration that Ilarion Reservoir has formed in a rocky area (canyon), this improvement in water quality suggests that it has entered in stabilization period approximately six years after its creation, earlier than the ten years period suggested by other studies [6, 42]. This highlights the importance of site selection in the construction of water reservoirs for hydroelectric energy production, since both specific morphology and absence of anthropogenic activities can lead to a good water quality only a few years after inundation of an area.

According to the results of *FTSI*, Polyfytos and Ilarion Reservoirs are classified as oligotrophic through mid-eutrophic waterbodies, with Ilarion Reservoir presenting better trophic state than Polyfytos (Table 5). This is in accordance with the previous results of *YΔΩPWQI*, where young Ilarion Reservoir exhibited better water quality indicative of its stabilization.

The respective average specific CO_2 and CH_4 emissions in Polyfytos Reservoir are 391.9 mg m^{-2} d^{-1} and 13.3 mg m^{-2} d^{-1} and in Ilarion Reservoir 389.8 mg m^{-2} $d^{-1}$and 4.6 mg m^{-2} d^{-1}. The emissions of CO_2 and CH_4 were relatively low in both Polyfytos and Ilarion Reservoirs, regardless their age difference, presenting non-significant statistical (*t*-test) difference in terms of specific CO_2 emission rate (Sig. = 0.499) and specific CH_4 emission rate (Sig. = 0.985). Nevertheless, Polyfytos Reservoir, exhibited three times higher productivity in terms of specific CH_4 emission rate when compared to Ilarion emissions. This is attributed to the relatively flat area with fertile soils that was impounded and to agricultural and livestock activities that increase inflow of organic matter in the reservoir contributing to higher GHGs emissions [43]. GHGs specific emissions from these two in-line reservoirs were also calculated in our previous work [24] for collected data of the years 2014-2016. During this period, it was found that the average specific CO_2 emission rate was 563.3 and 496.3 mg m^{-2} d^{-1}, whereas the average specific CH_4 emission rate was 38.5 and 28.9 mg m^{-2} d^{-1} in the case of Polyfytos and Ilarion respectively. Two years after the 2014-2016 monitoring period, the lower GHGs emissions measured in Ilarion Reservoir (see Table 5), as well as the limited biomass impoundment (canyon-like rocky area) indicate that this reservoir has reached its stabilization period, which is in accordance with the results obtained from the comparison of water quality indices between the two reservoirs. The fact that Ilarion Reservoir has entered its stabilization period only six years after its formation renders the selection of the reservoir location a crucial parameter on the assessment of how green is an investment on hydroelectric energy.

In Zazari Lake the respective average specific CO_2 and CH_4 emissions are 309.7 mg m^{-2} d^{-1} and 673.4 mg m^{-2} d^{-1}. Zazari natural lake (a) exhibits “Poor” water quality according to *YΔΩPWQI*, reflecting the degradation of organics due to domestic wastewater disposal (five years ago) from nearby villages (b) is characterized as hypereutrophic lake and (c) exhibits significantly higher GHGs emissions, especially regarding CH_4 emissions comparing with Ilarionas and Polyphytos Reservoirs (Sig. = 0.043 and Sig. = 0.033 respectively). It is worth mentioning that, despite the relatively low depth at Zazari Lake sampling station (4.5 m to 6 m) methanogenesis occurred at significantly high rates (mean value 673.4 mg m^{-2} d^{-1}). This is attributed to the hypertrophic state of Zazari Lake, which results in the creation of anoxic conditions, enhancing anaerobic biological processes [44]. Davidson et al. (2015) also found that nutrients concentration in a shallow eutrophic lake, such as Zazari Lake, have a profound effect in GHGs emission [45]. Domestic pollution of Zazari Lake ceased five years ago. Considering the significantly higher CH_4 emissions of Zazari Lake, as well as the deteriorated water quality and trophic state compared to that of Polyfytos and Ilarion Reservoirs, it is concluded that Zazari Lake can be characterized as a young artificial reservoir that has not yet been stabilized.

According to the results of this study, Ilarion Reservoir has entered its stabilization period (lower emissions) six years after its formation, while Zazari Lake five years after domestic pollution ceased still emits significant quantities of GHGs. Consequently, both morphology and anthropogenic activities affect the stabilization time of a waterbody.

According to Spearman statistical test, temperature presents strong positive correlation with CH_4 specific emissions (Corr. Coef. = 0.727, Sig. < 0.001) and GWP (Corr. Coef. = 0.823, Sig. < 0.001), indicative of the positive effect of temperature on methanogenesis.

On the other hand, CO_2 specific emissions present significant negative correlation with turbidity (Corr. Coef. = 0.728, Sig. < 0.001), a parameter that is indicative of the presence of microorganisms in a waterbody. This negative correlation as well as the absence of a similar strong negative correlation between CO_2 emissions and chlorophyll *α* shows that the presence of autotrophic microorganisms play a major role in carbon fixation by assimilating CO_2 [46]. The growth of chemolithotrophic bacteria that can fixate CO_2 or/and oxidise CH_4 could be triggered by the increased availability of specific nitrogenous nutrients, as indicated by the strong positive correlation (Sig. < 0.03) between turbidity and ammonium, nitrites and nitrates. Furthermore, the strong negative correlation of sulphates with the emission rates of CO_2 (Corr. Coef. = -0.964, Sig. = 0.001) and CH_4 (Corr. Coef. = -0.794, Sig. = 0.008), as well as the positive correlation of sulphates with turbidity (Corr. Coef. = 0.420, Sig. = 0.037) indicate the presence of sulphate reducing chemolithotrophs and their effect on CO_2 fixation and CH_4 oxidation [46].

3.3. Variability of GHGs emissions and statistical interpretation

The strong relation between carbonic GHGs emissions and seasonal changes of temperature is also evident in Figure 2 regarding the study area at North-

West Greece. The average water temperature of the studied waterbodies was 7.2 °C to 14.8 °C during the colder period (November to March), while during the warmer period (April to October) ranged from 18.8 °C to 25.1 °C. These differences in temperature result in a seasonal pattern regarding GWP of the waterbodies. As it can be seen from Figure 2, GWP increases in warmer period, when both CO_2 and CH_4 emissions are recorded, whereas it decreases in colder period due to methanogenesis inhibition and the sole production of CO_2. This seasonal pattern is also observed in CH_4 emissions, but is not observed in CO_2 emissions which are greatly affected by the presence of algae (carbon fixation) and a plethora of physicochemical parameters, such as salinity, pH, alkalinity and water temperature [47]. Interestingly, GWP is steeply increased, following CH_4 specific emissions in warmer period, further confirming the results of statistical process.

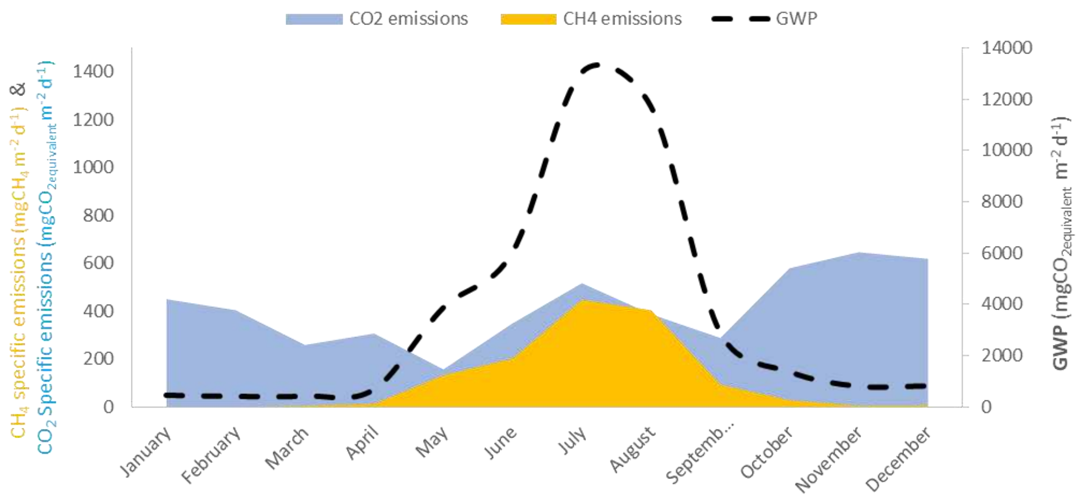

Figure 2. Monthly average specific emission rates* and GWP* of Ilarion, Polyfytos and Zazari sampling stations. **calculated from current (2018) measurement data (present study) and older (2014 to 2016) measurement data* [24]

The emissions of CO_2 and CH_4 from Zazari Lake follow the same seasonal pattern with that of GWP, but they were quantitatively higher than those of Polyfytos and Ilarion Reservoirs (Table 5). Negative CO_2 emissions where observed in Zazari Lake, which are attributed to the increased microbial activity in the hypereutrophic Zazari Lake and the subsequent carbon fixation. Compared to that of oligotrophic-mesotrophic lakes of Ilarion and Polyfytos, Zazari Lake exhibits up to 14 times more Chlorophyll *a* concentration and significantly worse water quality attributed to domestic pollution from neighboring villages. Thus, seasonal GHGs emissions of a waterbody and especially of a hypertophic one, should be assessed in terms of CH_4 emissions or/and GWP in order to count for the impact of microbial activity on GHGs emissions.

The statistical correlation between *YΔΩPWQI*, *FTSI* and the parameters expressing GHGs emissions i.e., GWP, specific CO_2 emissions and specific CH_4 emissions, revealed the link between water quality, trophic state and GHGs emissions.

In more detail, water quality in terms of *YΔΩPWQI* presented strong positive correlation (Spearman test, Sig.<0.05) with GWP (Cor. Coef. = 0.645, Sig. = 0.022) and specific CH_4 emissions (Corr. Coef. = 0.621, Sig. = 0.031). *FTSI* presents strong positive correlation with GWP (Corr. Coef. = 0.813, Sig. = 0.012) and specific CH_4 emissions (Corr. coef. = 0.823, Sig. = 0.008). Neither *YΔΩPWQI* nor *FTSI* presented statistical correlation with specific CO_2 emissions, which as mentioned in previous section is only correlated negatively with turbidity, an indicator of biological growth. The aforementioned results further support the use of CH_4 specific emissions as an indicator for the assessment of GWP that a waterbody exhibits.

4. Conclusions

According to trophic state index, both the six years old Ilarion Reservoir, as well as the forty-three years old Polyfytos Reservoir are classified as oligotrophic through mid-eutrophic reservoirs with "Good" water quality characterization. On the other hand, Zazari Lake, which is considered as a five years old reservoir, is classified as a hypereutrophic Lake with "Poor" water quality characterization.

The application of the water quality index revealed that water quality of Ilarion Reservoir is better than of Polyfytos Reservoir, characterized as "Good", whereas water quality of Polyfytos Reservoir is characterized as "Fair". Zazari Lake exhibited the worst water quality, characterized as "Poor". These results highlight the impact of reservoir's topography and of anthropogenic pressures on trophic state, water quality and the subsequent stabilization time of a reservoir.

The emissions of CO_2 and CH_4 were relatively low in Ilarion and Polyfytos Reservoirs. Both reservoirs presented non-significant statistical difference in terms of specific emissions and water quality, despite the fact that Polyfytos Reservoir exhibited three times higher specific CH_4 emissions and worst water quality according to the applied indices. On the contrary, Zazari Lake presented significant statistical differences compared to Ilarion and Polyfytos Reservoirs, both in terms of specific emissions and water quality exhibiting one to two orders of magnitude higher CH_4 emissions and two to three classes better water quality respectively.

Water quality and trophic state indices exhibited strong positive correlation with GWP and more specifically with specific CH_4 emissions. On the contrary, no statistical correlation between either indices and CO_2 specific emissions was found, as a result of carbon fixation. The strong positive correlation between GWP, specific CH_4 emissions and temperature justifies the steep increment of GWP in warmer period, with CH_4 emissions contributing up to 97% of the waterbodies' GWP, depending on seasonal water temperature variations.

Consequently, CH_4 specific emissions, as well as *YΔΩPWQI* and *FTSI* can be used as indicators for the assessment of GWP that a waterbody exhibit. Quantifying this relation may result in the creation of a rapid GWP assessment tool for researchers and engineers involved in fresh water and reservoir management.

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