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Centennial Assessment of Greenhouse Gases Emissions of Young and Old Hydroelectric Reservoir in Mediterranean Mainland

E. Amanatidou[1 *], G. Samiotis[1], E. Trikoilidou[1], L. Tsikritzis[1], and N. Taousanidis[2]

[1] Department of Chemical Engineering, University of Western Macedonia, Kozani 50100, Greece
[2] Department of Mechanical Engineering, University of Western Macedonia, Kozani 50100, Greece

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ABSTRACT. The quantities of emitted greenhouse gases (GHG) from hydroelectric reservoirs around the world, especially in warm latitudes, have tarnished the green credentials of hydroelectric energy. The accurate measurement and evaluation of the emitted GHG, which is a critical element in climate change policy, present a significant challenge. Many works have been focused on GHG emissions assessment from reservoirs around the world, but there are no available data concerning reservoirs in Mediterranean countries. In this study, emitted GHG from a young and an old in line water reservoirs, located in Mediterranean mainland, were collected using a "static floating chamber". Methane and carbon dioxide concentrations were measured and their specific emission rates were calculated. The data were used for the development of a mathematical prediction model, proposed for GHG emission assessment. Statistical correlation of GHG emissions and water physicochemical characteristics led to the interpretation of the biochemical processes taking place into the reservoirs. Furthermore, the impact of reservoir's morphology on GHG emissions was recorded, enhancing its importance on decision making for "green" energy investments. The results of this study indicate that artificial reservoirs in Mediterranean mainland generally have lower GHG emissions than those located in tropical and subtropical climatic zones and higher than those in continental subarctic zones and approach the highest values of CO_2 emissions and the mean CH_4 emissions recorded in continental climatic zones. The applied methodology provides a comprehensive tool for the long term (centennial) emissions assessment and the assessment of reservoirs impacts on the environment.

Keywords: carbon dioxide fluxes, climate change, floating chamber, hydroelectric dam, methane fluxes, reservoir morphology, water reservoir

1. Introduction

The three main greenhouse gases contributing to the global warming and thus to the climate change, are carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) (Goldenfum, 2012). The global warming potential (GWP) of CH_4 is considered more than 20 times higher than that of CO_2, on a molecule basis, as it can absorb infrared radiation more efficiently, over a 100 to 150 year period, increasing the anthropogenic contribution to the climate change (Perera et al., 2004; Thomson and Tanapat, 2005; Demarty and Bastien, 2011; Yang et al., 2014). According to UNESCO/IHA (2008) N_2O has an even higher GWP, on average 265 to 298 times higher than that of CO_2 for a 100-year timescale.

The increase in energy demand, in combination with the depletion of fossil fuels and the existing concern about greenhouse gases (GHG) emissions, have included hydroelectricity among the so called "green" energies (Demarty and Bastien, 2011). Bates et al. (2008) claimed that hydroelectricity is a non-intermittent renewable energy and therefore could sustain the development of others. However, the creation of hydroelectric reservoirs has a considerable impact on water storage and distribution, water quality, carbon and nitrogen cycles, regional climate, and ecosystems (Jing and Chen, 2011). Furthermore, studies on GHG emissions from reservoirs, especially in warm latitudes, have tarnished the green credentials of hydroelectricity (Giles, 2006).

The organic matter present (autochthonous) or entering the reservoir (allochthonous) is decomposed by bacteria under aerobic or anaerobic conditions (i.e., absence of oxygen), producing mainly CO_2 and CH_4, which are emitted from the reservoir by diffusion or bubbles (Guerin et al., 2011). Diffusion is the predominant way of CO_2 emission (bubbles contribute less than 1%) due to the large solubility of CO_2 into the water (Rosa et al., 2003). On the other hand, CH_4 is mainly emitted via bubbles, while diffusion can account as a secondary way, approximately three times less than bubbles (Abril et al., 2005). N_2O production can occur both in anaerobic or in aerobic biological processes. According to different studies, N_2O emissions are very low compared to CO_2 and CH_4 emissions (Tremblay et al., 2005; Diem et al., 2012).

GHG emissions from reservoirs are different from natural water sources, like rivers and lakes, due to the footprint from

* Corresponding author. Tel.: +30 24610 68015; Fax: +30 24610 39682
E-mail address: eamanatidou@uowm.gr (E. Amanatidou).

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human activities required (land use change), in order to convert the terrestrial and aquatic ecosystems into large flooded areas (Goldenfum, 2012; Yang et al., 2012). Terrestrial systems can become sinks or emitters of GHG depending on parameters such as the soil characteristics, the biomass characteristics and quantity and the environmental conditions (Thomson and Tanapat, 2005). Teodoru et al. (2009) investigated the CO_2 emissions from small boreal streams (< 5 km) in Quebec during the ice-free season. They concluded that small streams, despite their low areal coverage, contributed 25% to the total aquatic carbon emissions. On the other hand, the forests are considered as CO_2 sinks. Therefore, accounting only for the total GHG measured at the reservoirs' surface lead to "gross" emissions estimates, while by taking into account the GHG emissions before the reservoir creation, the "net" emission is estimated (UNESCO/IHA, 2010; Demarty and Bastien, 2011).

Several studies have investigated the GHG emissions from reservoirs in many areas around the world, focusing mainly on reservoirs located in cold regions (Huttunen et al., 2002; Tremblay et al., 2005; Tremblay et al., 2009), in temperate regions (Del Sontro et al., 2010; Sobek et al., 2012; Yang et al., 2014) and in tropical regions (Chanudet et al., 2011; Guerin et al., 2011; Teodoru et al., 2012). Research is lacking for reservoirs in Mediterranean countries, like Greece, and in similar regions. The phenomena of GHG emissions from hydroelectric reservoirs need to be investigated in specific areas due to their unique characteristics that influence the total GHG emissions. Therefore, generalizations based on research from specific areas cannot be assumed valid for all areas.

The production of GHG can be affected by many parameters, such as: 1) substrate availability, i.e., the amount of easily degradable organic matter (St. Louis et al., 2000; Teodoru et al., 2009); 2) temperature: elevated temperatures enhance the GHG emissions (Demarty and Bastien, 2011; Yang et al., 2014); 3) pH: the formation of bicarbonate is built up at basic conditions resulting in undersaturation of dissolved CO_2 and thus stimulating the absorption of atmospheric (Soumis et al., 2004; Tremblay et al., 2005); 4) reservoir age: the emissions decrease as a function of reservoir age, due to decline of available organic matter (St. Louis et al., 2000; Yang et al., 2014); 5) wind speed: strong winds promote the release of dissolved gases from the water surface (Cole and Caraco, 1998); 6) dissolved oxygen (DO): as DO concentration decreases with depth it enhances CH_4 emissions (Kosolapov, 2002; Xing et al., 2005); 7) algal growth: it has a negative impact on CO_2 emission fluxes and is affected by sunlight (Neal et al., 1998; Huang et al., 2015).

In cases of in line reservoirs located in a specific area, many of the parameters that affect GHG production are similar, thus giving an opportunity to evaluate the impact of the differentiating parameters (reservoir specificities) on GHG emissions. This study presents such a case of GHG emissions assessment of two in line water reservoirs in Mediterranean mainland (Aliakmon River, Western Macedonia, Greece) that were created for hydroelectric energy production. The assessment is based on the measured CH_4 and CO_2 emissions, the measurement of some water quality characteristics and the reservoirs' specificities, such as age and morphology. The study aims to bridge the existing gap in literature concerning GHG emissions from Mediterranean climatic zones and to indicates some of the critical parameters affecting GHG emissions, such as reservoir morphology, that have to be taken under serious consideration in decision making, concerning "green" energy investments.

2. Materials and Methods

The methodological approach of this work consists of: a) in-situ measurements of CH_4 and CO_2 fluxes using a "static floating chamber", b) measurement of the water physicochemical characteristics and b) statistical analysis between GHG emissions of the two reservoirs as well as between their water physicochemical characteristics.

2.1. Study Area

The study covers the area of the first two in line dams downstream Aliakmon River in Western Macedonia, Greece (Figure 1). Aliakmon River has a length of 310 km, its springs are located in the Grammos and Vernon mountains in North-Western Greece and discharges into the Thermaikos gulf, near Thessaloniki. In the area under consideration two water reservoirs were formed. The first reservoir downstream Aliakmon River (Ilarion), named as "young", has been recently created (2012), while the second (Polyfytos), named as "old", was created approximately forty two years ago (1973). Both reservoirs were created by the Greek Public Power Company (PPC) for energy production. Agricultural, livestock and limited industrial activities characterize the aforementioned area. The volume of Polyfytos and Ilarion reservoirs is 2,244 × 10^6 m^3 and 412 × 10^6 m^3, while their surface is 74 and 21.9 km^2, respecttively.

The climate of this Mediterranean area is transitional continental-Mediterranean with cold and dry winters, hot and dry summers and a precipitation of less than 950 mm. According to the data obtained from the Greek Ministry of Agriculture (Ministry of Agriculture, 1998), the warmest month of the year is July, with an average temperature of 21.6 °C and the coldest is January, with an average temperature of 0.6 °C. According to previous studies prior to and following the Ilarion reservoir formation (Ministry of Agriculture, 1998; Samiotis et al., 2018), the water flow from Aliakmon River to the reservoirs increases during the period of November to May, with a maximum flow in March (mean value 96 $m^3 \cdot sec^{-1}$) and decreases during the period of June to October, with a minimum flow in August (mean value 5.24 $m^3 \cdot sec^{-1}$). There are limited recorded cases of ice cover in the studied reservoirs, mainly in some shallow shores. Furthermore, there is a significant difference in water level fluctuations between the two reservoirs. According to two years monitored data, the highest measured depth in Polyfytos reservoir was 22 m, while in Ilarion reservoir 65 m and the water level fluctuations were approximately 5 and 15 m respectively. This differentiation occurs due to the morphological differences of each reservoir. Polyfytos Reservoir flooded a relatively flat area, creating a wide and swallow lake, while Ilarion reservoir was created in stiff rocky hills, forming a deeper canyon-like lake (Figure 1 and Supplementary Material). From Figure 1, where the terrain slopes are depicted, is obvious that Polyfytos Reservoir is located in an area of 0 to 15 degrees of terrain slope, while Ilarion reservoir terrain slopes range between 15 to 45 degrees.

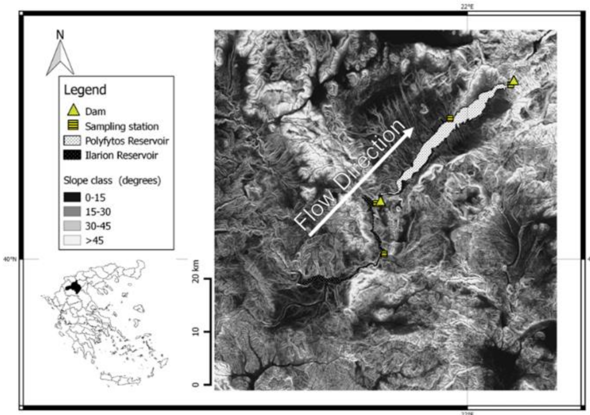

Figure 1. Study area and terrain slope classes (in degrees).

The filling of the recently created Ilarion Reservoir has resulted in flooding large areas of terrestrial and natural aquatic ecosystems. According to the conducted environmental impact study, from the 21.9 km^2 of flooded area, approximately 23.1% was river, 53.03% was non-forest soil (grassland, rocks and agricultural land) and 23.96% was forest (plane and oak trees) that was cleared prior to the reservoir flooding (Topiotechniki, 1994).

2.2. Sampling Schedule, Stations and Apparatus

The investigation of water quality in the study area started in July 2014 and continued up to August 2016. Two sampling stations were selected in each reservoir (Figure 1); the first one in the back of each dam (Ilarion Dam and Polyfytos Dam sampling stations) and the second one approximately 10 km upstream Ilarion and Polyfytos dam respectively (Ilarion Glossa and Polyfytos NOK sampling stations), taking into account the depth and the accessibility of the site. Depth is important in order to assure that anoxic conditions for biological methanogenesis in the hypolimnion are preserved. Monthly acquired GHG emission samples and water samples were collected in each sampling station during the first 17 months of monitoring and bimonthly GHG emission samples were collected from February 2016 until August 2016, leading to a total collection of 84 gas samples and 168 water samples (one from the surface and a second from a certain depth).

The sampling stations were approached by inflatable paddle boat and the selection of each chamber deployment site was made based on measurements of depth, to assure anoxic conditions in the hypolimnion (depth > 12 m up to 16 m). Gas samples were collected in relatively impermeable, multi-layered foil bags, suitable for gases collection. The bags were connected to the custom-made floating static chamber's one-way extraction valves (Figure 2). The floating static 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. The samples were collected by pumping (pressing downwards the static chamber) after 0, 50, 90, 130, and 180 min time since the chamber deployment. Gas samples were analyzed on the same day, using a calibrated gas chromatographer equipped with TCD/FID detector (Shimadzu GC-8A).

Surface (30 cm bellow water surface) and in depth water samples (approximately 1 m over specific sites' reservoir bottom) were collected according to ISO 5667-6 and analyzed using standard methods (Rice et al., 2012) at the ISO 17025 accredited Laboratory of Environmental Chemistry & Wastewater Treatment, of Environmental Engineering and Pollution Control Department, Western Macedonia University of Applied Sciences.

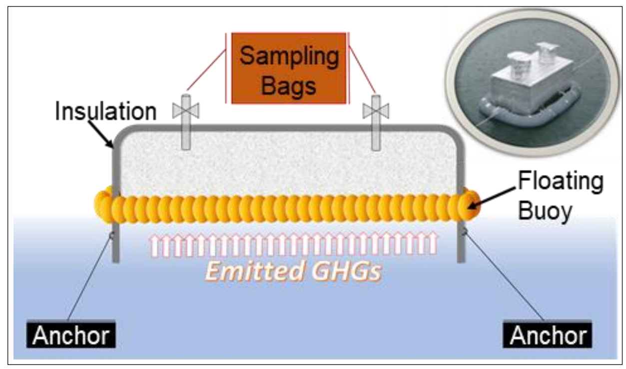

Figure 2. Configuration of floating static chamber for GHG emissions measurement.

The water physicochemical parameters analyzed, were: chemical oxygen demand (COD), biochemical oxygen demand (BOD), total kjeldahl nitrogen (TKN), ammonia, nitrite, nitrate, total suspended solids (TSS), pH, turbidity, color, conductivity, and alkalinity. The mean parametric values of the surface and in depth water samples were used in this study for the statistical correlation. Furthermore, in-situ temperature measurements of depth and surface water samples, as well as DO concentration at a depth of approximately 0.30 m, were taken in each sampling area, using calibrated instruments. Air temperature inside the chamber was also recorded.

The parameters of COD, BOD, TKN, Ammonia, Nitrite, and Nitrate are considered nutrients for a variety of flora and fauna species and their correlations can indicate pollution sources (autochthonous or allochthonous) that alternate reservoirs' water quality (Teodoru et al., 2009). Furthermore, their correlation with TSS, Turbidity and Color can help in the identification of plant residue dialysis decomposition phenomena (Amanatidou et al., 2014). The measurement of water temperature is considered of high importance as it is the mostly affected parameter by seasonal changes and it greatly affects the biochemical processes rates, such as methanation in hypolimnion (Teodoru et al., 2009). Changes of DO concentrations can indicate biochemical processes occurring in the reservoir (nitrification, organic compounds oxidation, etc.) and extreme pollution incidents (accidental or intentional). Finally, floating chamber's air temperature is essential in order to calculate GHG production using the ideal gases equation.

The measured GHG emissions and the measured water quality characteristics were statistically processed using "IBM SPSS Statistics 20" statistical software. The data normality was checked by using Shapiro – Wilk test and eventually non parametric statistical tests were chosen. In order to identify any significant spatial differences between the reservoirs' GHG emissions from the different sampling stations, Mann Whitney One-way ANOVA test ($p < 0.05$) was used. Furthermore, correlation between the measured emissions and the water physicochemical characteristics was performed (Spearman $p < 0.05$), in an attempt to link the measured water quality parameters with the produced GHG.

2.3. CO_2 and CH_4 Emissions Calculation

The CO_2 and CH_4 concentration measurements were used for the specific GHG emission rates calculation, according to equation (1) (Zheng et al., 2011; Brooker et al., 2014):

$$C=\rho \times \frac{dC}{dt} \times \frac{273.15}{(273.15+T)} \times H \tag{1}$$

where C is the specific gas emission rate ($mg \cdot m^{-2} \cdot h^{-1}$); ρ is the gas density in standard state ($kg \cdot m^{-3}$); dC/dt is the linear regression (LR)-based on slope of the chamber gas concentration versus time; H is the height (m) from the chamber top to the water surface; T is the air temperature (°C) inside the chamber.

2.4. CO_2 and CH_4 emissions prediction

Many process-based empirical models have been proposed in order to assess GHG emissions throughout reservoir's lifetime. Empirical models are used for net GHG emission evaluation using systematic measurements, while their combination with process-based models that are used for gross GHG emissions can improve their predictive capacity (UNESCO/IHA, 2008). In this study the approach of Delmas and Galy-Lacaux (2001) has been chosen, for the empirical formula creation (Equation (2)) that better describes the observed seasonal variations of emitted GHG on a monthly step. The Delmas and Galy-Lacaux (2001) formula was modified by implementing a phase shift factor. The decay constant of the formula is the variable used for model calibration and was estimated in each case in order to better-fit the measured emissions curve. It is worth mentioning that the resulting formula is applicable for all GHG, in our case for both CH_4 and CO_2:

$$GHG_{emission} = X_1 + X_2 \times \cos\left[\frac{2\pi}{12} \times (t - X_3)\right] \times e^{-X_4 \cdot t} \tag{2}$$

where $GHG_{emission}$ ($mg \cdot m^{-2} \cdot d^{-1}$) is the specific emission rate prediction; t (months) is the reservoir age; X_1 ($mg \cdot m^{-2} \cdot d^{-1}$) is the initial value of methane fluxes; X_2 ($mg \cdot m^{-2} \cdot d^{-1}$) is the amplitude of the prediction curve; X_3 (months) is the horizontal shift or phase shift of the prediction curve; X_4 ($months^{-1}$) is the exponential decay constant.

A discrete equation was created for each of the measured GHG (CH_4 and CO_2) and for each reservoir. In order to accurately describe the recorded emissions in the young (Ilarion) and the old (Polyfytos) reservoirs and to validate the prediction model, experimental data obtained from the sampling areas (511 to 534 months and 19 to 44 months since Polyfytos and Ilarion reservoirs formation respectively) were used. Taking into account that the initial values of each GHG emission (X_1), i.e., after the reservoir impoundment, are considered to be higher than of those measured during the study period, the following assumptions were made:

The highest measured mean emission value, calculated as the mean value between reservoir's sampling stations at that specific date, is the initial emission value (X_1) in each created equation.The amplitude of the prediction curve (X_2) is considered as the difference between the lowest and the highest mean emission value of each sampling area measurement set (both sampling stations of each reservoir).The phase shift factor (X_3) in each prediction equation corresponds to the date of the highest mean emission value, in order to express the seasonal GHG emissions as well as their magnitude.

3. Results and Discussion

3.1. Temporal and Spatial Variations of GHG and Temperature

In Figures 3 to 5, the temporal and spatial variations of CO_2, CH_4 and the temperature of each sampling station of the two reservoirs can be seen. The same behavior can be seen in all sampling stations and in both reservoirs. The lowest values of CO_2 emissions are measured during summer, while of CH_4 are during winter. The CO_2 emissions increase gradually during autumn, reaching the highest values in winter, while during spring a gradual decrease is observed. In all sampling stations, the CO_2 fluxes presented significant temporal variation (Mann Witney $p < 0.05$) and insignificant spatial variation (Mann Witney $p > 0.05$), even between Ilarion Reservoir (constructed in 2012) and Polyfytos Reservoir (constructed in 1974). Similarly to CO_2 emissions, the CH_4 emissions presented significant temporal variation (Mann Witney $p < 0.05$) and insignificant spatial variation (Mann Witney $p > 0.05$). However, a different trend can be seen for CH_4 emissions compared to those of CO_2. The gradual increase of CH_4 emissions starts during spring reaching the highest values in summer, while during autumn gradual decrease is observed. The seasonal global warming potential follows the CH_4 emissions pattern, due to the high methane's GWP (28 times of CO_2 for a 100 years period). The highest GWP values are obtained when maximum CH_4 fluxes are recorded (August to September) and are calculated using the CH_4 GWP coefficient of 28 (UNESCO/IHA, 2008). The lowest GWP values are obtained when methane fluxes are zero (February to March) and are equal to CO_2 emissions (GWP coefficient of CO_2 is 1). The statistical descriptive of the GHG fluxes and temperature measurements is presented in Table 1.

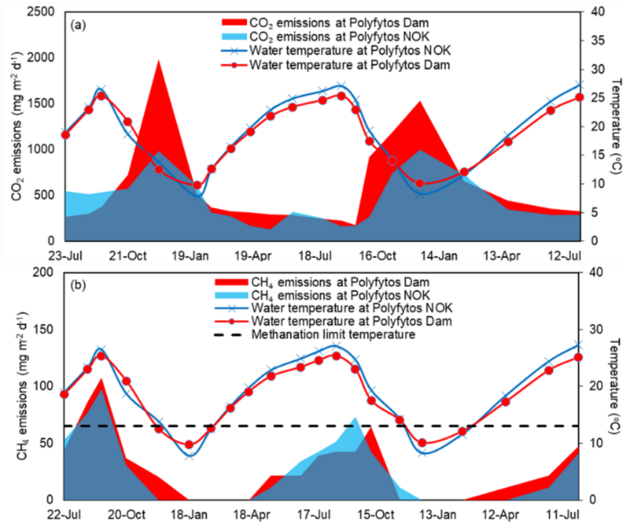

Figure 3. Temporal and spatial variations of (a) CO_2 and (b) CH_4 emissions at Polyfytos Reservoir's sampling stations in relation to water temperature.

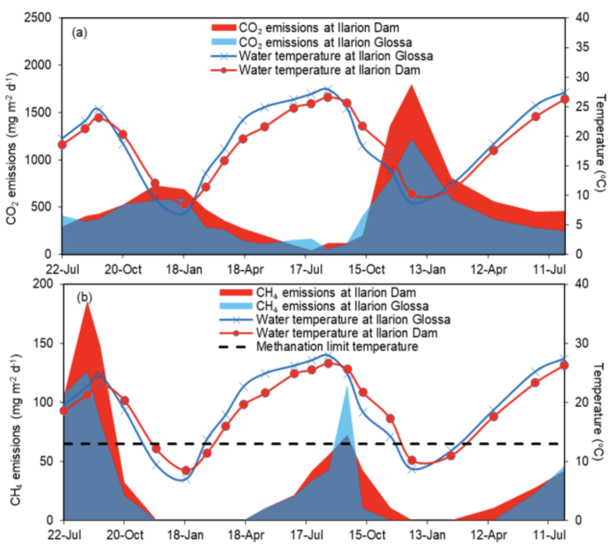

Figure 4. Temporal and spatial variations of (a) CO_2 and (b) CH_4 emissions at Ilarion Reservoir's sampling stations in relation to water temperature.

Generally, higher GHG emissions are expected during the first years of a reservoir formation compared to those of the later years. This is due to the initial high organic substrate availability (flooded organic residues) that provides the necessary compounds for biochemical reactions, producing CO_2 and CH_4 (Neal et al., 1998; Huang et al., 2015). Consequently, one will expect that the young reservoir (Ilarion) will have higher GHG emissions than the older reservoir (Polyfytos). However, the recorded GHG emissions were similar in both reservoirs. A satisfactory explanation for this observation is that relatively low quantities of plant residues have been impounded, because of the morphology of Ilarion Reservoir and deforestation of the area. On the other hand, the old reservoir flooded a relatively flat area with fertile soils, where for agricultural and livestock activities occurred (see section 2 of supplementary material).

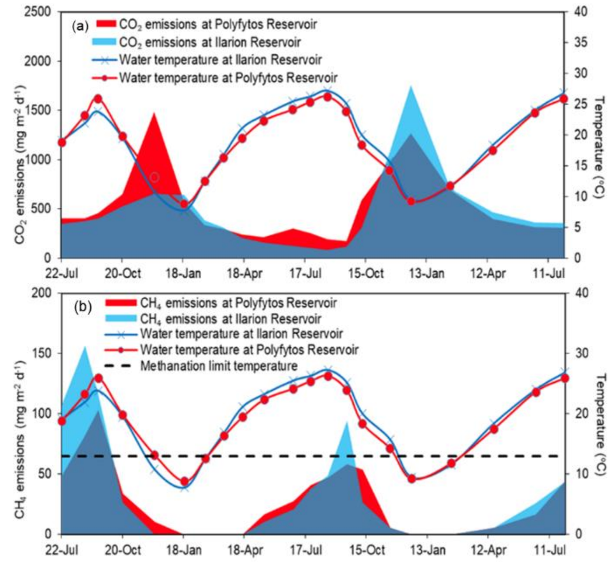

Figure 5. Temporal and spatial variations of (a) CO_2 and (b) CH_4 emissions at Polyfytos Reservoir and at Ilarion Reservoir in relation to average water temperature.

Although, morphological characteristics differ between the aforementioned reservoirs, an estimation of the flooded soil's organic matter quantities is made, based on (a) reservoir surface; (b) the measured organic content of the surface soil layer in the reservoirs' area (approximately 5% in Polyfytos and 3% in Ilarion); (c) the bulk density of soils (Polyfytos 1.12 $g \cdot cm^{-3}$ and Ilarion 1.28 $g \cdot cm^{-3}$) (Topiotechniki, 1994). In this estimation the impoundment of plant residues is not taken into account, as there are no available data concerning the vegetation of Polyfytos area prior flooding. The calculated impounded organic matter in Polyfytos and Ilarion Reservoir is 1.2432×10^6 and 2.52288×10^5 kg respectively. This difference would be greater if there were available data concerning the depth of the surface soil layer in Ilarion Reservoir, which would be less than Polyfytos due to landscape morphology, i.e., stiff and rocky hills compared to the arable land of Polyfytos (Samiotis et al., 2018). Consequently, Polyfytos Reservoir, which has five times the amount of flooded organics than that of Ilarion Reservoir, is expected to emit more GHG and that is the reason why similar emission rates are observed in both reservoirs, despite their age difference of almost forty years.

3.2. Centennial GHG Assessment

A long term (centennial) assessment of the emitted GHG was performed based on the measured GHG fluxes, as the 100 years period is considered to be the life cycle of a reservoir (Delmas and Galy-Lacaux, 2001). The CH_4 emissions from Polyfytos Reservoir are expressed by Equation (3), which derived from equation (2) and uses the calculated factors from the available measurement data (Table 2). Subsequently, CO_2 emissions from Polyfytos Reservoir can be expressed by Equation (4), CH_4 emissions from Ilarion Reservoir by Equation (5) and the CO_2 emissions from Ilarion Reservoir by Equation (6):

$$PolyfytosCH_{4emission} = 102.9 + 102.9 \times \cos\left[\frac{2\pi}{12} \times (t - 8.45)\right] \times e^{-0.002t} \tag{3}$$

$$PolyfytosCO_{2emission} = 1484.9 + 1308.9 \times \cos\left[\frac{2\pi}{12} \times (t - 11.19)\right] \times e^{-0.0012t} \tag{4}$$

$$IlarionCH_{4emssion} = 156.4 + 156.4 \times \cos\left[\frac{2\pi}{12} \times (t - 7.84)\right] \times e^{-0.04t} \tag{5}$$

$$IlarionCO_{2emssion} = 1760.0 + 1672.7 \times \cos\left[\frac{2\pi}{12} \times (t - 11.72)\right] \times e^{-0.015t} \tag{6}$$

In Figure 6, the graphical illustration of Equation (3) and Equation (4) is presented, in comparison to measured emissions (a, c), as well as the emissions assessment, on a monthly step for a 100 years period (b, d).

In Figure 7, the graphical illustration of Equations (5) and (6) is presented, in comparison to measured emissions (a, c), as well as the emissions assessment, on a monthly step for a 100 years period (b, d).

The CH_4 and CO_2 emissions differ among different reservoirs, depending on substrate availability, meteorological conditions, water physicochemical characteristics, reservoir's age and on reservoir's biology (Cole and Caraco, 1998; Neal et al., 1998; St. Louis et al., 2000; Kosolapov, 2002; Soumis et al., 2004; Treblay et al., 2005; Xing et al., 2005; Teodoru et al., 2009; Demarty and Bastien, 2011; Yang et al., 2012; Huang et al., 2015). There are not any emission measurements from reservoirs, natural lakes or rivers concerning the Mediterranean countries. Measurements at lakes and reservoirs in continental climate (British Columbia and Quebec Canada, Southeast Poland, Switzerland, Austria) have recorded CH_4 emissions from 0.14 to 3850 $mg \cdot m^{-2} \cdot d^{-1}$ and CO_2 emissions from 25 to 7150 $mg \cdot m^{-2} \cdot d^{-1}$ (Tremblay et al., 2005; Linde and Wildman, 2013). In subtropical and tropical areas (China, South America) CH_4 fluxes from 0.744 to 3240 $mg \cdot m^{-2} \cdot d^{-1}$ and CO_2 fluxes from 475 to 10400 $mg \cdot m^{-2} \cdot d^{-1}$ have been measured (Rosa et al., 2003; Chen et al., 2011; Wang et al., 2011; Jiang et al., 2012; Yang et al., 2013; Mosher et al., 2015), while in continental subarctic fluxes (Finland , Sweden) were from 3.5 to 1800 $mg \cdot m^{-2} \cdot d^{-1}$ and from 1070 to 2076 $mg \cdot m^{-2} \cdot d^{-1}$ respectively (Podgrajsek et al., 2013; Soja et al., 2014). From the studies around the world it is obvious that there are significant differences of the emissions even at water bodies of the same climatic zone. So the investigation of as many as possible water bodies will help scientists

Table 1. Statistical Descriptive of GHG Measurements in All Sampling Stations

Statistical Descriptive	Polyfytos Dam Temperature (ºC)	CO_2 Fluxes ($mg \cdot m^{-2} \cdot d^{-1}$)	CH_4 Fluxes ($mg \cdot m^{-2} \cdot d^{-1}$)	Polyfytos NOK Temperature (ºC)	CO_2 Fluxes ($mg \cdot m^{-2} \cdot d^{-1}$)	CH_4 Fluxes ($mg \cdot m^{-2} \cdot d^{-1}$)
Min	9.8	179.3	0.0	7.8	131.1	0.0
Max	25.5	1983.8	107.9	27.3	1002.2	97.8
Average	18.8	563.3	28.9	19.4	438.4	27.5
Median	19.1	354.5	21.6	19.3	322.6	10.9
Std. Dev.	5.3	473.6	30.3	6.2	260.7	30.3
Samplings	21	21	21	21	21	21
	Ilarion Dam			Ilarion Glossa		
Min	8.5	46.0	0.0	7.0	58.1	0.0
Max	26.6	1804.3	185.8	27.9	1222.2	126.9
Average	19.2	496.3	38.5	19.6	383.1	30.6
Median	20.3	433.7	21.2	19.6	347.4	10.7
Std. Dev.	5.7	423.9	51.5	6.6	271.8	41.8
Samplings	21	21	21	21	21	21

Table 2. Factors Used for GHG Emission Rate Prediction Model

Greenhouse Gas	Reservoir Name	Initial Fluxes (X_1) ($mg \cdot m^{-2} \cdot d^{-1}$)	Curve Amplitude (X_2) ($mg \cdot m^{-2} \cdot d^{-1}$)	Phase Shift (X_3) (month)	Decay Constant (X_4)
Methane	Polyfytos	102.9	102.9	8.45	0.0020
(CH_4)	Ilarion	156.4	156.4	7.84	0.0420
Carbon Dioxide	Polyfytos	1454.9	1308.9	11.19	0.0015
(CO_2)	Ilarion	1760.0	1672.7	11.72	0.0150

to get more accurate conclusions of the GHG emissions from water bodies and their effect on global climatic change. The results of this study indicate that artificial reservoirs in Mediterranean mainland regions with similar to the study area climatic conditions, generally emit less than 225 mg·m^{-2}·d^{-1} of CH_4 (regardless reservoir's age) GHG, which is less than the emissions recorded in those located in tropical, and subtropical, continental and continental subarctic climatic zones more than continental subarctic zones. CO_2 emissions in the study area are lower than 3,000 mg·m^{-2}·d^{-1} (regardless reservoir's age), which are significantly lower than those from reservoirs in tropical, subtropical and continental climatic zones, while they do approach the highest values of CO_2 emissions and the mean CH_4 emissions, recorded in continental subarctic climatic zones.

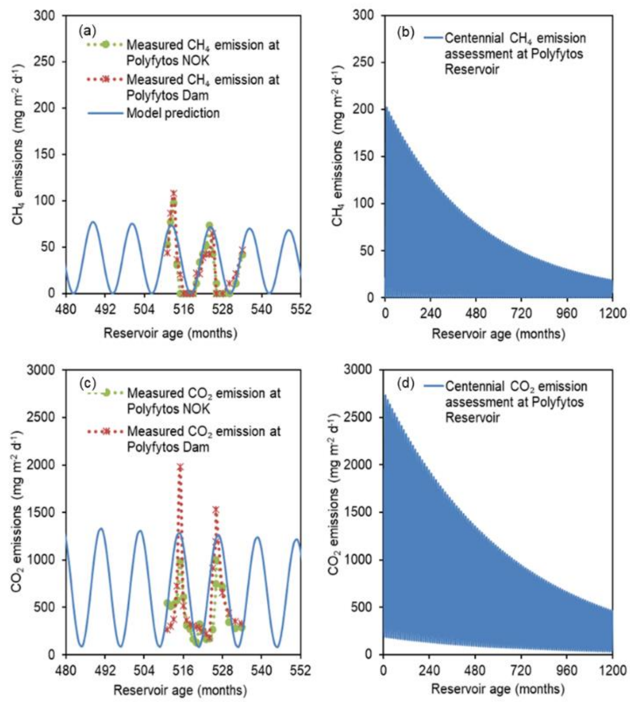

Figure 6. Assessment of CH_4 and CO_2 emissions at Polyfytos Reservoir.

3.3. Correlation of the Measure Water Quality Characteristics with GHG Emissions

The CH_4 emissions are strongly correlated with temperature (Spearmann, $p = 0.001$), as it was expected because of the linear or exponential relationship between temperature and methanogenic bacteria activity (Topiotechniki, 1994), while CO_2 emissions did not present such behavior (Spearmann, $p = 0.679$). Consequently, the reason behind the seasonal variation of CO_2 emissions is not the temperature variation, but probably the biochemical utilization of CO_2 by algae that bloom during warmer and sunniest seasons. This conclusion can be confirmed by similar observations of other studies, which also attributed these fluctuations of CO_2 emissions on freshwater algae photosynthesis and CO_2 fixation (Neal et al., 1998; Huang et al., 2015). There is a seasonal pattern in these fluctuations leading to higher algae presence during warmer months and significantly less during the colder months, as reported from previous studies concerning Aliakmon River and Polyfytos Reservoir (Tryfon and Moustaka-Gouni, 1997; Moustaka-Gouni et al., 2007; Vatalis et al., 2008). The enhancement of photosynthesis draws down the saturation levels of CO_2 in water, lowering water to air CO_2 emissions (Meyers, 1997). It is worth mentioning that most of fixed CO_2 by algal photosynthesis is later decomposed and emitted as CH_4 and therefore, it could more than offset any favorable effect of algal fixation (St. Louis et al., 2000).

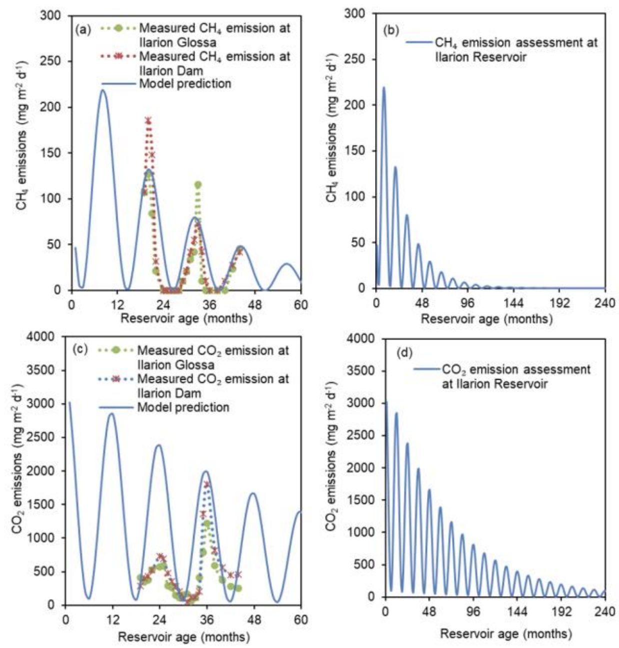

Figure 7. Assessment of CH_4 and CO_2 emissions at Ilarion Reservoir.

Concerning the correlation between the measured water quality characteristics and the measured GHG emissions, the statistical analysis revealed (a) significant positive correlation between water temperature and CH_4 production (Spearman, $CC = 0.727$, $p < 0.001$), (b) significant positive correlation between Organic and Ammonia with CO_2 production (Spearman, $CC = 0.675$, $p < 0.01$), (c) significant negative correlation between Color and CO_2 production (Spearman, $CC = -0.622$, $p < 0.05$) and (d) significant negative correlation between Nitrate ions and CH_4 production (Spearman, $CC = -0.705$, $p < 0.005$).

The interpretation of the statistical analysis results provides satisfactory explanations for the processes responsible for reservoirs GHG emissions. The (a) positive correlation between water temperature and CH_4 production was expected (Brooker et al., 2014). A satisfactory explanation behind the (b) strong positive correlation between organic and ammonia nitrogen with CO_2 emissions is that the degradation (hydrolysis) of animal and plant origin nitrogenous organic matter (urea, proteins, chlorophyll, etc) releases ammonia (ammonification) and low molecular weight organic molecules. The low molecular weight organic molecules are biochemically utilized, producing CO_2

and CH_4, at a higher rate than ammonia, due to the significantly lower utilization rate of nitrifying bacteria species and the required aerobic conditions for their activation. Furthermore, the color of the water is linked to algal growth that fixates CO_2 providing an explanation about (c), the negative correlation between Color and CO_2 production. The strong negative correlation between nitrates and temperature justifies the (d) negative correlation between nitrates and CH_4 production. More specifically, during the rainy and colder seasons, the water runoffs increase nitrate content in the reservoirs (Samiotis et al., 2018), while water temperature drops to levels that inhibit methanogenesis. Consequently, the correlation was strong not because of CH_4 and nitrate chemical or biochemical linkage, but because the water runoffs coincide with the temperature drop and the inhibition of methane production.

4. Conclusions

The study investigated the spatial and temporal variations of GHG emissions of a young and an old reservoir in Aliakmon River, Greece. Compared to other studied rivers and lakes in the world, the CH_4 GHG emissions from the two artificial reservoirs in Mediterranean mainland region were significantly lower than those located in tropical and subtropical, subtropical, continental and continental subarctic climatic zones climatic zones, while CO_2 emissions are significantly lower than those from reservoirs in tropical, subtropical and continental climatic zones, and approaching the highest values of CO_2 emissions and the mean CH_4 emissions recorded in continental subarctic climatic zones. From the assessment of the results it appears that the quantities of emitted GHG depend on reservoir morphology and that reservoir age influences the declining rate of the emission curve.

Seasonal behavior of CH_4 and CO_2 were recorded but are attributed to different factors. CH_4 variation is caused by increased activity of methanogenic bacteria, enhanced by higher temperatures, while CO_2 variation is caused by increased algal growth enhanced by prolonged sunlight. In the specific reservoirs, the physicochemical parameters that are significantly correlated with the emitted GHG are temperature, nitrate nitrogen, ammonia and organic nitrogen and color; consequently their usage for creating a prediction model should be evaluated.

From the results of the study, it is obvious the effect of morphology to the GHG emissions since the young but canyon like reservoir has similar emissions to the old but flat reservoir. It is essential to monitor these two Mediterranean reservoirs for the coming years, in order to further calibrate the assessment model and verify their long-term behavior. Morphology appears to be a critical parameter for GHG emissions and has to be taken under serious consideration during the planning and construction of new reservoirs in Mediterranean regions as elsewhere.

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