Variations in Greenhouse Gas Fluxes at the Water–Gas Interface in the Three Gorges Reservoir Caused by Hydrologic Management: Implications for Carbon Cycling

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Abstract: The Three Gorges Project is the largest hydraulic hub project in the world, and its hydrological management has altered the hydrological environment of the reservoir area, affecting the carbon emission and absorption of the reservoir water. In this study, representative hydrological stations in the Three Gorges Reservoir area were selected as research sites to monitor the CO₂ and CH₄ fluxes of the reservoir water and nine environmental factors during the drainage and impoundment periods in 2022. The study aimed to explore the mechanisms of hydrological management and environmental factors on greenhouse gas emissions. The results showed that the mean CO₂ fluxes of the reservoir water during the drainage and impoundment periods were $(103.82 \pm 284.86)$ mmol·m⁻²·d⁻¹ and $(134.39 \pm 62.41)$ mmol·m⁻²·d⁻¹, respectively, while the mean CH₄ fluxes were $(1.013 \pm 0.58)$ mmol·m⁻²·d⁻¹ and $(0.571 \pm 0.70)$ mmol·m⁻²·d⁻¹, respectively, indicating an overall “carbon source” characteristic. Through the evaluation of the characteristic importance of environmental factors, it was found that the main controlling factors of CO₂ flux during the drainage period were total phosphorus (TP) and chlorophyll a (Chl_a), while total nitrogen (TN) was the main controlling factor during the impoundment period. Dissolved organic carbon (DOC) was the main controlling factor of CH₄ flux during the different periods. Based on these findings, a “source-sink” mechanism of CO₂ and CH₄ in the Three Gorges Reservoir water under reservoir regulation was proposed. This study is of great significance for revealing the impact of reservoir construction on global ecosystem carbon cycling and providing scientific support for formulating “emission reduction and carbon sequestration” plans and achieving “dual carbon” goals.

Keywords: Three Gorges Reservoir; CO₂ flux; CH₄ flux; stable isotopes; random forest; influencing mechanism

1. Introduction

The carbon cycle is one of the most important material cycles in the Earth’s ecosystem, referring to the process of carbon migration and transformation among the Earth’s atmosphere, hydrosphere, lithosphere, pedosphere, and biosphere. It helps maintain the stability of the biosphere’s structure and functionality and is crucial for global material and energy cycles as well as climate change [1]. The concentration of CO₂ in the atmosphere is one of the main factors affecting global climate warming [2]. In today’s increasingly industrialized world, human activities have disrupted the balance of CO₂ exchange among various carbon reservoirs, leading to a more complex mechanism of CO₂ emissions. A significant portion of carbon in inland water bodies is transported to the ocean, both in dissolved and solid forms. Additionally, a fraction of this carbon (25% to 44%) is directly emitted into the
atmosphere as greenhouse gases, such as CO$_2$ and CH$_4$. [3]. The global inland water bodies emit approximately 2.1 PgC and 0.7 PgC of CO$_2$ and CH$_4$ gases to the atmosphere each year, respectively, while the global terrestrial ecosystems absorb approximately 2.6 PgC of carbon per year [4–6]. These two quantities are of the same order of magnitude, and their contributions to global climate change should not be ignored.

The construction of dams in rivers disrupts their continuity and alters the carbon sources and sinks in reservoirs. The construction of dams and subsequent reservoir impoundment has brought about a series of changes that have modified the temporal and spatial patterns of carbon exchange in the reservoir, giving rise to a distinct carbon cycling pattern within the reservoir. For example, dam impoundment increases the residence time of water, providing favorable conditions for the generation of endogenous carbon-containing substances and the degradation of organic matter [7]. The release of CO$_2$ from reservoir surfaces accounts for approximately 4% of all anthropogenic sources [8], and the annual emission of greenhouse gases from reservoirs to the atmosphere continues to increase [9,10]. With the accelerated pace of hydropower development, river dam construction technology is rapidly expanding worldwide. Currently, the total surface area of global dam reservoirs in rivers is approximately $1.5 \times 10^6$ km$^2$, which is comparable to the surface area of natural lakes. There are over 70,000 large dams, and the total volume of reservoirs is seven times that of natural rivers [11]. Water reservoirs are important facilities for storing and regulating water sources, and they are closely linked to the water distribution network (WDN) system. In the distribution network, the water network partitioning method is often used to improve the pressure performance of the WDN, with the aim of reducing water resource loss [12]. In the management and regulation process of large-scale water reservoirs, partitioned management is also required, so that the regulation of water reservoirs can reduce carbon emissions without affecting the domestic water use of residents, which is essential.

As the world’s largest hydraulic project, the Three Gorges Dam has attracted extensive attention from researchers in recent years regarding the carbon cycling process in its ecosystem. Some scholars believe that the Three Gorges Reservoir area will submerge a large number of plants growing in the fluctuation zone, which will decompose and produce a significant amount of greenhouse gases [13]. Other scholars argue that the Three Gorges Reservoir has unique characteristics in terms of deep-water river channels, and the pre-flooding reservoir-clearing work results in relatively low greenhouse gas emissions [14]. Additionally, the hydrodynamic conditions after impoundment enhance the growth of algae, contributing to carbon sequestration [15]. Previous studies on greenhouse gases in reservoirs have often focused on specific periods or individual factors, leaving significant gaps in understanding the mechanisms of greenhouse gas emissions in relation to hydrological management and environmental factors. This study takes the Three Gorges Reservoir area as an example and conducts on-site measurements and sample collection at ten hydrological stations within the reservoir area. By analyzing the spatiotemporal differences in greenhouse gas flux, the differences in the physicochemical properties of the water, and the effects of reservoir regulation, the study aims to identify the key processes and mechanisms influencing carbon sources and sinks. The goal is to provide a basis for accurately evaluating greenhouse gas emissions from the reservoir, develop emission reduction and carbon sequestration strategies, and contribute to the achievement of the “dual carbon” targets.

2. Materials and Methods

2.1. Study Area

The Three Gorges Dam is located at the lower end of the upstream Yangtze River (106°14′~111°28′ E, 28°56′~31°44′ N). It is a typical river-valley-type reservoir with steep slopes on both sides of the river channel [16]. The reservoir has a water surface area of 1080 km$^2$ and a storage capacity of up to 39.9 × 10$^6$ m$^3$ [17]. The Three Gorges Reservoir area covers 20 districts and counties, with a total area of 54,200 km$^2$. In the reservoir area, agriculture is primarily focused on crop cultivation and livestock farming [18]. The
upstream and middle reaches of the Three Gorges Reservoir area are mainly composed of sandstone and mudstone, while the downstream area is dominated by carbonate rocks and clastic rocks [19]. Of the area in the reservoir, 96% is mountainous, while 4% is plains. The main land use types are croplands and forests, accounting for 36.57% and 46.88%, respectively [20]. The operation and management of the dam follow the “storage and controlled discharge” strategy, which involves storing water in winter and discharging it in summer, resulting in a fluctuation zone with water levels fluctuating between 145 m and 175 m [21]. The reservoir region has a subtropical monsoon climate, with an average annual temperature of 17 °C and an average annual precipitation of 1250 mm [22].

2.2. Sample Collection and Field Measurements

Ten representative hydrological stations were selected within the Three Gorges Reservoir area, starting from Chongqing and extending to the Three Gorges Dam. These stations include Zhutuo (ZT), Zhongxian Shibaozhai (ZX), Mudong (MD), Fuling (FL), Wanzhou (WZ), Fengjie (FJ), Wushan (WS), Badong (BD), Xiangxi River Estuary (XXHK), and Maoping (MP). These locations cover the overall range of water storage in the Three Gorges Reservoir area. In the Three Gorges Reservoir area, the low water level corresponds to the drainage period in July, while the high water level corresponds to the storage period in December. Water samples were collected at the selected hydrological stations in July and December of 2022. Sampling started from the upstream and proceeded along the direction of the Yangtze River. Sampling was conducted on the banks adjacent to the hydrological stations. Each sampling event lasted approximately one week. The sampling sites are shown in Figure 1, The information for the Sampling sites is as shown in Table 1.
Table 1. Specific information on sampling sites.

<table>
<thead>
<tr>
<th>Sampling Points</th>
<th>Altitude (m)</th>
<th>Distance from the Previous Sampling Site (Km)</th>
<th>Maximum Annual Runoff</th>
<th>Minimum Annual Runoff</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZT</td>
<td>205</td>
<td>0</td>
<td>3179</td>
<td>1934</td>
<td>2591</td>
</tr>
<tr>
<td>ZX</td>
<td>163</td>
<td>166</td>
<td>4221</td>
<td>2479</td>
<td>3375</td>
</tr>
<tr>
<td>MD</td>
<td>171</td>
<td>13.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FL</td>
<td>171</td>
<td>115.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>WZ</td>
<td>166</td>
<td>165.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FJ</td>
<td>124</td>
<td>120.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>WS</td>
<td>134</td>
<td>43.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BD</td>
<td>141</td>
<td>47.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>XXHK</td>
<td>113</td>
<td>44.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MP</td>
<td>129</td>
<td>25.8</td>
<td>5442</td>
<td>2848</td>
<td>4173</td>
</tr>
</tbody>
</table>

Notes: The annual runoff data covers the period from 2000 to 2022, with units of 100 million cubic meters; "-" indicates that the relevant data has not yet been obtained.

At each sampling point, on-site measurements and sample collection of the water body were performed. The samples were collected at a depth of 30-50 cm below the water surface, and the water samples obtained were measured onsite for water quality parameters such as temperature (T), pH, dissolved oxygen (DO), and electrical conductivity (EC) using a Thermo Scientific Orion Star A320 series (Waltham, MA, USA) portable electrochemical meter. Surface water samples were collected using 5 L plastic buckets. On the same evening, the samples were filtered using a filtration pump. Different pretreatment methods were applied based on the specific parameters of interest. Total nitrogen (TN) samples were acidified to pH < 2 using H₂SO₄ (Zhongtian Chemical Co., Ltd, Wuhan, China). Total phosphorus (TP) samples were acidified to pH < 2 using HNO₃ (Zhongtian Chemical Co., Ltd, Wuhan, China). The water samples were filtered using pre-burned Whatman GF/F glass fiber membranes (0.7 µm) (Limin Industrial Co., Ltd, Shanghai, China) that were pre-soaked in 5% dilute HNO₃ overnight. The filtrate was stored in pre-burned glass bottles at 450 °C, and saturated HgCl₂ solution was added before sealing. The samples were stored at low temperatures for determination of dissolved organic carbon (DOC). The water samples were filtered using acetate fiber membranes (0.45 µm) (Limin Industrial Co., Ltd, Shanghai, China) in needle filters that were pre-soaked in 5% dilute HNO₃ overnight. The filtrate was stored in special bottles, and saturated HgCl₂ solution was added before storage at low temperatures for determination of dissolved inorganic carbon (DIC). After filtering the water sample with GF/C filters, the filters were stored in a freezer at −20 °C for determination of chlorophyll-a (Chl_a). The data on CO₂ and CH₄ gas flux in this study were obtained from the testing results of the “Hubei Key Laboratory of Intelligent Yangtze and Hydroelectric Science, China Yangtze Power Co., Ltd., Yichang, China”.

2.3. Analytical Methods

In the laboratory, the total nitrogen (TN) content in the water samples was determined using the alkaline potassium persulfate oxidation–ultraviolet spectrophotometric method. Total phosphorus (TP) was determined using the potassium persulfate oxidation–spectrophotometric method. Chlorophyll-a (Chl_a) was determined using the acetone extraction–spectrophotometric method. The concentrations of dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) in the water samples, as well as their corresponding isotopes, were analyzed at the Third Institute of Oceanography, Ministry of Natural Resources. The DOC content was determined using the iso TOC CUBE total organic carbon analyzer, which measures the corresponding peak area and calculates the DOC concentration of the sample. The DIC content was measured by preparing standard solutions of NaHCO₃ and Na₂CO₃ in a 1:1 mass ratio at different concentrations. The instrument measured the peak area and concentration, and a standard curve was plotted to calculate the DIC content of the sample. Stable carbon isotopes are represented by the
symbol “δ” and indicate the parts per thousand deviations of the isotope ratio in the sample relative to the isotope ratio of a standard sample:

$$\delta^{13}C = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$$  \hspace{1cm} (1)

where R is $^{13}C/^{12}C$ and $\delta^{13}C$ corresponds to international standard Pee Dee belemnite (PDB).

2.4. Data Analysis

Non-parametric tests were employed to determine the significant differences in environmental factors and greenhouse gas fluxes between the two periods. A Spearman correlation analysis was conducted to examine the relationships between the influencing factors and greenhouse gas fluxes in the Three Gorges Reservoir area during the drainage and storage periods. Heatmaps illustrating the correlation between greenhouse gas fluxes and environmental factors were generated. The contribution of each environmental factor to CO$_2$ and CH$_4$ fluxes, known as a feature importance assessment, was calculated using the random forest algorithm. This assessment involved computing the contribution value of each feature in every decision tree within the random forest. The Python 3.9 programming software was utilized, with the software framework based on the TensorFlow framework using the Keras deep learning tool. The RandomForestClassifier algorithm from the sklearn library was employed for the sensitivity analysis of relevant indicators and CO$_2$ and CH$_4$ fluxes, enabling the determination of the importance percentage of each indicator. By analyzing the data results, the mechanisms underlying the greenhouse gas emissions in the Three Gorges Reservoir could be explored. Figure 2 shows the flowchart of the study.

Figure 2. Flowchart of the study.

3. Results

3.1. Physicochemical Variations in the Surface Waters of the TGR

The physicochemical properties of the water in the Three Gorges Reservoir area are presented in Table 2. The pH values during the different periods ranged from 8.21 to 8.67 and 7.59 to 7.8, respectively. The pH was significantly higher during the drainage period compared to the water impoundment period ($p < 0.05$). This difference is attributed to changes in the hydrodynamic environment caused by water management practices, and the values at different sampling points exhibited relatively small fluctuations (Figure 3a). The water temperature (T) in the reservoir area ranged from 23.75°C to 25.35°C during the drainage period and from 15.08°C to 16.69°C during the water impoundment period. The
water temperature was significantly higher during the drainage period compared to the water impoundment period ($p < 0.05$), and the differences in T among different sampling points were relatively small (Figure 3b). The electrical conductivity (EC) of the water varied from 304.5 to 381 $\mu$S/cm during different periods and from 314.25 to 400.4 $\mu$S/cm during the water impoundment period. The EC was higher during the water impoundment period compared to the drainage period, and the seasonal differences were significant ($p < 0.05$). The fluctuations in EC at different sampling points were relatively small (Figure 3c). The dissolved oxygen (DO) levels ranged from 5.78 to 8.38 mg/L during different periods and from 8.42 to 9.78 mg/L during the water impoundment period. The DO levels were significantly higher during the water impoundment period compared to the drainage period ($p < 0.05$), and the fluctuations in DO at different sampling points were relatively small (Figure 3d).

Table 2. Physicochemical parameters of the surface water in the Three Gorges Reservoir area in the drainage and impoundment periods.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Drainage Period</th>
<th>Impoundment Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.21–8.67</td>
<td>7.59–7.8</td>
</tr>
<tr>
<td>T/°C</td>
<td>23.75–25.35</td>
<td>15.08–16.69</td>
</tr>
<tr>
<td>TN/mg·L$^{-1}$</td>
<td>1.58–2.49</td>
<td>1.26–1.56</td>
</tr>
<tr>
<td>TP/mg·L$^{-1}$</td>
<td>0.06–0.504</td>
<td>0.05–0.07</td>
</tr>
<tr>
<td>DO/mg·L$^{-1}$</td>
<td>5.78–8.38</td>
<td>8.42–9.78</td>
</tr>
<tr>
<td>DOC/mg·L$^{-1}$</td>
<td>4.59–9.02</td>
<td>1.63–2.94</td>
</tr>
<tr>
<td>DIC/mg·L$^{-1}$</td>
<td>2.77–6.76</td>
<td>12.04–27.88</td>
</tr>
<tr>
<td>Chl_a/µg·L$^{-1}$</td>
<td>1.53–69.41</td>
<td>0.25–1.07</td>
</tr>
<tr>
<td>EC/µS·cm$^{-1}$</td>
<td>304.5–381</td>
<td>314.25–400.4</td>
</tr>
</tbody>
</table>

**Figure 3.** Distribution of environmental factors of the surface water in the Three Gorges Reservoir area, pH (a), T (b), EC (c), DO (d), TN (e), TP (f), DOC (g), DIC (h), and Chl_a (i), respectively.
The total nitrogen (TN) concentration in the water of the Three Gorges Reservoir area during the drainage period ranged from 1.58 to 2.49 mg/L, while during the water impoundment period, it ranged from 1.26 to 1.56 mg/L. The TN concentrations exhibit slightly greater fluctuations during the drainage period compared to the water impoundment period. This can be attributed to the decrease in water level during the drainage period, which results in less hydraulic connectivity among different spatial locations and leads to certain differences in water sources [23]. The total phosphorus (TP) concentrations during the two periods ranged from 0.06 to 3.17 mg/L and 0.05 to 0.07 mg/L, respectively. TN and TP exhibited significant differences between the two periods ($p < 0.05$). These differences are attributed to various factors, such as soil properties, human activities, and variations in hydraulic conditions of the water body during different periods (Figure 3e,f).

During the drainage period and water impoundment period, the concentration range of dissolved organic carbon (DOC) in the water was 4.59–9.02 mg/L and 1.63–2.94 mg/L, respectively. The mean values were (6.29 ± 1.54) mg/L and (2.16 ± 0.28) mg/L, respectively. The DOC concentration during the drainage period was slightly higher than the global average of 5.75 mg/L for rivers [24]. This difference is likely attributed to various factors such as human activities, plant decomposition, and hydrological processes. The DOC concentration was significantly higher during the drainage period compared to the water impoundment period ($p < 0.05$). The concentration range of dissolved inorganic carbon (DIC) during different periods was 2.77–6.76 mg/L and 12.04–27.88 mg/L, with mean values of (4.96 ± 1.35) mg/L and (23.54 ± 5.39) mg/L, respectively. The DIC concentration was significantly higher during the water impoundment period compared to the drainage period ($p < 0.05$).

The chlorophyll-a (Chl_a) concentration during different periods ranged from 1.53 to 69.41 µg/L and 0.25 to 1.07 µg/L, with mean values of (14.13 ± 22.17) µg/L and (0.60 ± 0.24) µg/L, respectively. The Chl_a concentration was significantly higher during the drainage period compared to the water impoundment period ($p < 0.05$). This difference is related to the geographical location and climatic conditions of the Three Gorges Reservoir. During the drainage period, there were significant spatial variations in Chl_a concentration, with higher values downstream of the reservoir, which to some extent affects the greenhouse gas emissions in the reservoir area. In contrast, the Chl_a content during the water impoundment period was very low with small fluctuations (Figure 3i).

3.2. Carbon Isotope Characteristics

The $\delta^{13}C$ is commonly used to analyze the source of carbon in water bodies. Studies have shown that the carbon isotope composition in the main stream of the Yangtze River does not exhibit significant seasonal variations [25]. Therefore, carbon isotope testing in this study was only conducted on water samples during the drainage period. The test results are shown in Table 3. The range of $\delta^{13}C_{DOC}$ in the sampled points within the reservoir area was $-32.61\%$ to $-30.11\%$, with an average value of $-31.35\%$. The range of $\delta^{13}C_{DIC}$ in the water samples from the reservoir area was $-7.96\%$ to $-4.89\%$, with an average value of $-6.72\%$. There was not a significant difference between the $\delta^{13}C_{DOC}$ and $\delta^{13}C_{DIC}$ values in the sampled points. The analysis of $\delta^{13}C$ is crucial for further determining the sources of carbon in the water bodies within the reservoir area.

<table>
<thead>
<tr>
<th>Sampling Points</th>
<th>$\delta^{13}C_{DOC}/%$</th>
<th>$\delta^{13}C_{DIC}/%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZT</td>
<td>$-31.80$</td>
<td>$-4.89$</td>
</tr>
<tr>
<td>ZX</td>
<td>$-30.86$</td>
<td>$-6.01$</td>
</tr>
<tr>
<td>MD</td>
<td>$-30.34$</td>
<td>$-5.55$</td>
</tr>
<tr>
<td>FL</td>
<td>$-32.57$</td>
<td>$-7.25$</td>
</tr>
<tr>
<td>WZ</td>
<td>$-32.61$</td>
<td>$-7.96$</td>
</tr>
<tr>
<td>FJ</td>
<td>$-30.84$</td>
<td>$-7.56$</td>
</tr>
<tr>
<td>WS</td>
<td>$-31.31$</td>
<td>$-7.81$</td>
</tr>
</tbody>
</table>
3.3. Spatiotemporal Variation of Greenhouse Gas Fluxes

The average CO₂ fluxes during the two periods were 103.82 ± 284.86 mmol·m⁻²·d⁻¹ and 134.39 ± 62.41 mmol·m⁻²·d⁻¹, respectively. From Figure 4a, it can be observed that the CO₂ flux exhibited a “source” characteristic during the drainage period. The CO₂ flux was significantly higher at the “WZ” and “WS” points, while it was negative (indicating CO₂ uptake) at the “ZT” and “MP” points, indicating a CO₂ “sink”. During the impoundment period, the CO₂ flux at the “MP” within the reservoir exhibited relatively small variations and remained stable as a CO₂ “source”. However, compared to the drainage period, the CO₂ flux significantly decreased, and at the BD point, it showed a CO₂ “sink” characteristic. There was no significant difference in CO₂ flux between the different periods (p > 0.05).

Figure 4. Spatial and temporal variation of CO₂ flux (a) and CH₄ flux (b) in the Three Gorges Reservoir area.

The average CH₄ fluxes during the drainage period and the impoundment period were 1.013 ± 0.58 mmol·m⁻²·d⁻¹ and 0.571 ± 0.70 mmol·m⁻²·d⁻¹, respectively. Figure 4b shows that the CH₄ flux exhibited a “source” characteristic during both the drainage and impoundment periods, with higher CH₄ fluxes at the “ZX” and “MD” sampling points during the impoundment period compared to the drainage period. Overall, there was a significant seasonal difference in CH₄ flux, with significantly higher fluxes during the drainage period than the impoundment period (p < 0.05).

3.4. Correlation of Environmental Factors

3.4.1. Hydrochemical Factors

The correlation heatmap between the greenhouse gas flux and environmental factors is shown in Figure 5. During the drainage period, there was a positive correlation between the water temperature (T) and CO₂ in the water, while during the impoundment period, they exhibited a negative correlation. On one hand, the high temperature during the drainage period can increase microbial activity in the water, leading to an increase in CO₂ emissions [26,27]; on the other hand, during the impoundment period, the decrease in water temperature and the stabilization of the water body result in reduced nutrient input at the bottom of the water, leading to a decrease in the abundance of phytoplankton. As a result, the dominance of respiratory decomposition processes in the water persists [28]. Although the CO₂ flux during the impoundment period is weaker than that during the drainage period, it still exhibits a CO₂ “source” characteristic. In both periods, there was a negative correlation between T and CH₄ flux, with higher CH₄ flux during the drainage period compared to the impoundment period. This finding differs from previous
High temperatures can promote CH$_4$ production [24,29], and lower water levels and stronger hydraulic conditions during the drainage period are more conducive to CH$_4$ oxidation [30,31]. The reason for the discrepancy in this study is primarily that the high temperature during the drainage period promotes CH$_4$ production but is offset by increased water flow and oxygen availability, while the low temperature during the impoundment period inhibits methane production but is offset by higher water levels and lower dissolved oxygen. The relatively small variations in CH$_4$ flux between different periods in this study indicate that hydrological management in the reservoir plays a significant role in greenhouse gas emissions.

Figure 5. Heat map of the correlation between the greenhouse gas fluxes and each indicator during the drainage period (a) and the impoundment period (b); the number marked in the figure represents the correlation coefficient; red symbolizes a positive correlation, while blue represents a negative correlation.
pH can affect the CO₂ concentration in the water by altering the equilibrium (CO₂ + H₂O ⇌ H₂CO₃ ⇌ H⁺ + HCO₃⁻ ⇌ 2H⁺ + CO₃²⁻) [32]. As pH increases, the water can absorb more CO₂. Therefore, pH is negatively correlated with CO₂ flux in different periods. During the drainage period, pH is negatively correlated with CH₄ flux, whereas the opposite relationship is observed during the impoundment period. Methanogenic archaea thrive at pH levels ranging from 6.5 to 7.8, and they are typical anaerobic microorganisms [33]. In this study, the pH of the water during the drainage period was relatively higher than the optimal pH range for methanogenic archaea, which could reduce CH₄ flux to some extent. However, during the impoundment period, the pH of the water was suitable for the growth of methanogenic archaea, which could facilitate CH₄ production to a certain extent.

The relationship between dissolved oxygen (DO) and CO₂ in water is primarily influenced by the combined effects of photosynthesis and respiration. On one hand, photosynthesis by plants can convert inorganic carbon in the water into organic carbon, thereby reducing CO₂ concentration and flux. On the other hand, respiration in the water consumes dissolved oxygen. In theory, these processes should exhibit an inverse relationship [34]. However, in this study, the correlation between DO and CO₂ flux was weak. The relationship between DO and CH₄ flux varied in different periods. In theory, DO in water is unfavorable for the survival of methanogenic archaea. However, during the impoundment period, there was a positive correlation between DO and CH₄ flux. This may be attributed to the limitation of the collected samples in this study, which were surface water samples and may not fully reflect the DO conditions in the deeper parts of the water body. Additionally, the correlation between electrical conductivity (EC) in water and greenhouse gas flux was relatively weak in this study.

3.4.2. Nutrient Factors

During the drainage period, total nitrogen (TN) and total phosphorus (TP) showed an overall positive correlation with greenhouse gas flux. On one hand, TN and TP can provide favorable conditions for the growth of phytoplankton in the water, which can then utilize photosynthesis to absorb greenhouse gases. On the other hand, when phytoplankton die, they provide a carbon source for microbial decomposition, leading to the release of more greenhouse gases. TN and TP also provide favorable conditions for microbial proliferation in the water, enhancing greenhouse gas emissions. In the assessment of lake impacts, nutrient ratios in the water, specifically the TN/TP ratio, can indicate nutrient limitation for algal growth. A TN/TP ratio above 20:1 indicates phosphorus limitation, while a ratio below 13:1 indicates nitrogen limitation [35]. In this study, during the drainage period, the growth of phytoplankton was to some extent limited by nitrogen availability.

During the impoundment period, TN showed a weak correlation with CO₂ and CH₄ flux, while TP exhibited a positive correlation with CO₂ flux and a negative correlation with CH₄ flux. During the impoundment period, the TN/TP ratio in the water was greater than 20:1, indicating that the growth of phytoplankton was to some extent limited by phosphorus availability. The weak correlation between TN and TP with greenhouse gas fluxes during this period can be attributed to environmental factors such as temperature (T) and dissolved oxygen (DO), which suppress microbial activity and subsequently affect greenhouse gas emissions. Additionally, the differences in TN/TP ratio between different periods are influenced by the release processes of nitrogen and phosphorus in the water. Specifically, during the drainage period, phosphorus is more easily released from sediments, while during the impoundment period, nitrogen is more likely to be obtained from water and soil runoff in the reservoir area. The specific processes are detailed in Section 4.2 of the study.

3.4.3. Carbon Source Factors

There is no significant correlation between dissolved organic carbon (DOC) content and the emission of CO₂ gas in the reservoir water. Although carbon sources play a role in greenhouse gas emissions from the perspective of element conversion and material
conservation, there are many factors that collectively influence the conversion of carbon sources into CO$_2$ gas. Dissolved inorganic carbon (DIC) in the water, which directly exchanges with CO$_2$ gas in the atmosphere, shows opposite correlations in different periods. The reason for this can be attributed to the high temperature during the drainage period. On one hand, the carbonate equilibrium reaction in the water tends to shift towards the production of CO$_2$ gas. On the other hand, higher temperatures decrease the solubility of gases in the water. Additionally, the lower water level during the drainage period leads to a significant positive correlation between inorganic carbon and CO$_2$ gas flux. In contrast, during the impoundment period with lower temperatures and higher water levels, a certain negative correlation is observed.

During the drainage period, there is a significant positive correlation between DOC and methane (CH$_4$) flux, while the correlation is weaker during the impoundment period. The production of CH$_4$ gas is closely related to anaerobic methane-producing bacteria. The high temperature during the drainage period enhances the utilization of DOC by methane-producing bacteria, leading to the production of CH$_4$ gas [36]. However, the production of CH$_4$ is largely influenced by reservoir hydrological management, resulting in relatively small fluctuations in CH$_4$ flux in different periods. There is no direct connection between DIC and methane-producing bacteria, and there is no significant correlation between DIC in the water and CH$_4$ gas flux.

3.4.4. Chlorophyll-a

During the drainage period, Chl$_a$ (chlorophyll-a) and CO$_2$ flux exhibit a negative correlation, while during the impoundment period, they show a positive correlation. In the downstream water of the reservoir during the drainage period, the Chl$_a$ content is much higher than in the upstream and midstream areas. This results in higher primary productivity in this region compared to the respiratory activities of organisms and microbes. This is an important reason why the downstream “MP” in the reservoir acts as a CO$_2$ sink and contributes to the negative correlation between Chl$_a$ and CO$_2$ flux. During the impoundment period, dam construction and water regulation lead to the homogenization of water areas [36], resulting in a relatively uniform spatial distribution of Chl$_a$ during this period. However, the lower temperatures and nutrient limitations during the impoundment period may affect the photosynthetic activity of the water, leading to a negative correlation between Chl$_a$ and CO$_2$ flux during the impoundment period.

Chl$_a$ and CH$_4$ flux are negatively correlated during the drainage period. The higher Chl$_a$ levels in the downstream area of the reservoir during this period indicate higher photosynthetic activity, resulting in increased dissolved oxygen in the water. This, to some extent, inhibits the activity of methane-producing bacteria and reduces CH$_4$ production. However, during the impoundment period, Chl$_a$ and CH$_4$ flux show a positive correlation, which contradicts expectations. Previous studies suggest that after the death of phytoplankton, they become a carbon source in the water, providing favorable conditions for methane-producing bacteria [37]. Additionally, the rise in water levels during reservoir impoundment submerges a large amount of vegetation in the littoral zone, providing conditions for the proliferation of anaerobic methane-producing bacteria. These factors contribute to the observed positive correlation between Chl$_a$ and CH$_4$ flux during the impoundment period.

4. Discussion

4.1. Sources of Carbon in the Waters of the Three Gorges Reservoir Area

The range of $\delta^{13}$C$_{DOC}$ values for different source end-members is summarized in Table 4. The $\delta^{13}$C$_{DOC}$ range in the reservoir water was between $-32.61\%$ to $-30.11\%$, which is comparable to the $\delta^{13}$C range of phytoplankton ($-42\%$ to $-24\%$) and C3 plant-synthesized organic carbon ($-38\%$ to $-23\%$). Thus, it is suggested that a significant portion of the organic carbon in the reservoir water originates from phytoplankton and terrestrial C3 plants, indicating the influence of agricultural activities in the Three Gorges.
Reservoir area on organic carbon in the water. Previous studies have also shown that terrestrial C3 plants are a major source of organic carbon in water. For example, in Canada’s Lake Mackenzie, the primary supply of DOC comes from terrestrial C3 plants, while contributions from aquatic plants account for only about 15%. Similarly, in thermal karst lakes, the main source of DOC is also terrestrial plants [38].

Dissolved inorganic carbon in water bodies primarily originates from the following sources: CO$_2$ in soil (including the decomposition of soil organic matter and silicate rocks), carbonate rock minerals, and atmospheric input through precipitation [39]. In the Yangtze River Basin, soil CO$_2$ is derived from the oxidation of organic matter and undergoes diffusion, with a range of $\delta^{13}$C values from $-30.2\%$ to $-19.8\%$ [40–42]. After soil CO$_2$ dissolves in water, the range of $\delta^{13}$C$_{DIC}$ should be $-21.8\%$ to $-10.8\%$, with an average value of $-17\%$ [43,44]. The dissolution of carbonate rocks can be categorized into sulfate-driven carbonate dissolution and carbonic acid-driven carbonate dissolution. For sulfate-driven carbonate dissolution, the $\delta^{13}$C$_{DIC}$ is solely derived from the carbonate itself. In carbonic acid-driven carbonate dissolution, two distinct DIC components with different isotopic compositions are produced in equal amounts. One component originates from soil CO$_2$, and the other component originates from the mineral itself. Marine carbonate rock minerals exhibit a $\delta^{13}$C enrichment range of approximately $-3.33\%$ to $2.44\%$, with a mean value of around $0\%$ [45,46]. The contribution of DIC from atmospheric precipitation is relatively low and is typically neglected. The contribution of DIC sources in water bodies can be calculated based on the principle of mass balance:

$$\delta^{13}C_{car} \times R_c + \delta^{13}C_{CO_2} \times R_s = \delta^{13}C_{DIC} \quad (2)$$
$$R_c + R_s = 1 \quad (3)$$

where $\delta^{13}C_{car}$, $\delta^{13}C_{CO_2}$, and $\delta^{13}C_{DIC}$ represent the $\delta^{13}$C values of carbonate rock dissolution, soil CO$_2$, and the DIC in the reservoir water, respectively. $R_c$ and $R_s$ represent the proportions of DIC derived from carbonate minerals and soil, respectively. The average value of $\delta^{13}$C$_{DIC}$ in the water body is $-6.72\%$. By simultaneously solving Equations (1) and (2), the proportions of DIC derived from carbonate rock minerals and soil CO$_2$ can be obtained as 60.47% and 39.53%, respectively.

Table 4. The $\delta^{13}$C distribution of the different end-members.

<table>
<thead>
<tr>
<th>Organic Carbon End-Member</th>
<th>$\delta^{13}$C (V-PDB, %)</th>
<th>Reference</th>
<th>Inorganic Carbon End-Member</th>
<th>$\delta^{13}$C (V-PDB, %)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>$-26--23$</td>
<td>[47]</td>
<td>Soil CO$_2$</td>
<td>$-21.8--10.8$</td>
<td>[43,44]</td>
</tr>
<tr>
<td>Sewage</td>
<td>$-28.5--23$</td>
<td>[51–53]</td>
<td>Atmosphere</td>
<td>$-8--6$</td>
<td>[40]</td>
</tr>
<tr>
<td>Vascular Plant</td>
<td>$-30--16$</td>
<td>[47,54]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C3 Plants</td>
<td>$-38--23$</td>
<td>[46]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C4 Plants</td>
<td>$-17--9$</td>
<td>[55]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.2. The Assessment of Feature Importance for Environmental Factors

This study utilized the random forest algorithm to calculate the contribution of various influencing factors to CO$_2$ and CH$_4$ fluxes in the Three Gorges Reservoir. Specifically, the feature importance assessment was conducted [56]. By inputting the different influencing factors as independent variables and CO$_2$ and CH$_4$ fluxes as the dependent variables into the random forest algorithm, the contribution rates of each influencing factor to greenhouse gas fluxes during different periods were obtained (Figure 6). During the drainage period, the main controlling factors for CO$_2$ flux were TP and Chl$_a$ with contribution rates of 26.47% and 16.86%, respectively. In the impoundment period, TN was the main controlling factor for CO$_2$ flux with a contribution rate of 25.14%. T, Chl$_a$, and pH had
contribution rates of around 16%. The higher pH, temperature, and growth of algae and other phytoplankton during the drainage period can cause the release of a large amount of phosphorus from sediments [57]. In the impoundment period, high water levels can result in significant nitrogen loss from the reservoir soil into the water [58], leading to an increase in the N/P ratio in the water. Both nitrogen and phosphorus are essential elements for microbial cytoplasm synthesis, gene transcription, and protein synthesis in the water. The changes in the N/P ratio due to the increase in different nutrients in the reservoir promote the proliferation of different types of microorganisms, leading to the decomposition of carbon sources in the water. For example, researchers have conducted experiments on nitrogen–phosphorus imbalance in sludge, and the results showed that under P limitation, the growth of Proteobacteria in the sludge increased to some extent [59]. Another study found that abundant filamentous bacteria proliferated in wastewater when nitrogen was deficient and phosphorus was sufficient [60]. Therefore, the main controlling factors for CO₂ flux vary during different periods in the reservoir.

![Graph showing the contribution rates of each influencing factor to greenhouse gas flux in the water of the Three Gorges Reservoir](image)

**Figure 6.** The contribution rates of each influencing factor to greenhouse gas flux in the water of the Three Gorges Reservoir, (a) representing CO₂ flux and (b) representing CH₄ flux.

The main controlling factor for CH₄ flux during both the drainage period and the impoundment period is DOC, with contribution rates of 33.06% and 21.16%, respectively. The primary source of CH₄ in the water is the anaerobic decomposition of organic carbon by methane-producing bacteria. DOC, as a direct carbon source for microorganisms, is a key factor in controlling CH₄ production. It is worth noting that in both periods, DIC has the second-highest contribution to CH₄ flux, with a contribution rate of 16.33% during the impoundment period. Theoretically, DIC has a relatively small impact on CH₄ production in the water. However, its higher contribution rate is likely related to the process of methane production. The process of CH₄ production in the water involves a complex microbial food chain, in which certain microbial groups decompose organic carbon into intermediate products for methane-producing bacteria to further break down, leading to the release of a large amount of inorganic carbon into the water environment. Therefore, the process of CH₄ production is often accompanied by the generation of a significant amount of inorganic carbon, resulting in the relatively high contribution of DIC to CH₄ flux.

4.3. *Exploration of the Mechanisms of Greenhouse Gas Emissions in Reservoirs*

The main biogeochemical processes related to carbon cycling in the reservoir water involve aerobic respiration of animals, plants, and microorganisms, photosynthesis of green phytoplankton, and anaerobic respiration of microorganisms. Aerobic respiration involves the breakdown of carbohydrates and occurs primarily through glycolysis and
the tricarboxylic acid cycle. The key enzymes involved in these reactions are glucokinase and phosphofructokinase [61]. In general, the optimal pH range for most microorganisms for these enzymes is between 6 and 8, and the suitable temperature is around 35 °C. The pH levels in the reservoir water during different periods are generally suitable for these enzymes. The higher temperature during the drainage period favors enzyme activity and promotes these reactions. The low water level and strong hydraulic conditions during the drainage period create a more aerobic environment for microorganisms in the water, leading to increased synthesis and activity in these enzymes. This, in turn, promotes cellular energy production and the respiratory chain process. Nitrogen (N) and phosphorus (P) in the water can facilitate microbial synthesis of cellular material, gene transcription, and protein synthesis, thereby promoting the decomposition of organic matter by microorganisms.

The process of photosynthesis involves two stages: the light reaction and the carbon fixation reaction [61]. Key elements in this process include pigment synthesis and CO₂ fixation. The former requires light energy, nitrogen, phosphorous, and the participation of Mg²⁺, while the latter requires RuBP to fix CO₂. The optimal temperature and pH for these reactions are between 15 °C and 35 °C and between 6 and 7.5, respectively. The higher pH during the drainage period has a relatively minor impact on these reactions. The higher temperature during the drainage period promotes photosynthesis, and sufficient light ensures chlorophyll synthesis, making photosynthesis stronger during this period compared to the impoundment period. During the impoundment period, low temperatures and insufficient light may lead to the death of phytoplankton in the water, turning them into organic matter for microbial decomposition and enhancing greenhouse gas emissions. Nitrogen (N) and phosphorous (P) in water can promote photosynthesis.

The anaerobic respiration process occurs in an anaerobic digestion system and involves a four-stage theory comprising fermentation bacteria, hydrogen and acetate-producing bacteria, homozygous acetogenic bacteria, and methane-producing bacteria [62]. This process relies on organic matter in the water as a substrate, thus highlighting the significant impact of dissolved organic carbon on CH₄ production. During the drainage period, the higher pH of the water may partially inhibit the activity of methane-producing bacteria, but the elevated temperature easily promotes the aforementioned reactions. In contrast, during the impoundment period, the pH of the water is more suitable for the survival of methane-producing bacteria. The stable hydraulic conditions and slightly anaerobic environment during this period facilitate CH₄ production. However, the low temperature during the impoundment period may partially inhibit CH₄ production. Additionally, another important factor influencing CH₄ flux is the hydrological management of the reservoir, which largely offsets the effects of temperature and DOC on the methane production process, resulting in relatively small fluctuations in CH₄ flux during different periods.

The Three Gorges Dam utilizes a water management approach known as “storage and controlled discharge”, which leads to lower water levels and increased water flow during the drainage period. This dynamic flow condition during the drainage period accelerates the degradation of organic matter and suspended particles in the water. As a result, the pH of the water is relatively higher compared to the impoundment period. In contrast, during the impoundment period, the water flow in the reservoir is reduced, allowing substances to accumulate. This slower flow rate during the impoundment period leads to slower degradation of organic matter and suspended particles, potentially resulting in their accumulation in the water and promoting the generation of acidic substances, thereby lowering the pH of the water. Water management also affects the nutrient elements in the water. During the drainage period, phosphorus is more easily released from sediment, while nitrogen during the impoundment period originates from agricultural pollution to some extent within the reservoir area. Therefore, there are differences in the nutrient element content in the water during different periods. The external conditions during different periods also influence the growth of phytoplankton and other aquatic organisms, leading to significant differences in Chl_a concentration. Plant growth is more favorable during the drainage period, resulting in significantly higher Chl_a concentration compared
to the impoundment period. In summary, during the drainage period, temperature, N, and P elements have a promoting effect on the involved biogeochemical processes in the water. Dissolved oxygen has opposite effects on aerobic and anaerobic respiration, and photosynthesis shows a certain degree of nitrogen limitation. Anaerobic respiration is also partially inhibited by pH. During the impoundment period, temperature restricts all biogeochemical processes in the water, while N and P elements promote these processes. Photosynthesis exhibits phosphorus limitation. DO continues to have opposite effects on aerobic and anaerobic respiration, and its low concentration promotes methane production. Dissolved organic carbon in the water serves as a substrate for both aerobic and anaerobic respiration, promoting these respiratory processes during both periods. Water management also influences methane production processes. Therefore, during the drainage period, photosynthesis and aerobic respiration are more active, while anaerobic respiration is less active compared to the impoundment period. Figure 7 illustrates the influencing mechanisms of greenhouse gas flux in the Three Gorges Reservoir area.

**Figure 7.** The impact mechanism of hydrological management on greenhouse gas emissions in the Three Gorges Reservoir.

### 5. Conclusions

This study evaluates the distribution and spatiotemporal variations of environmental factors, carbon isotopes, and greenhouse gas fluxes in the Three Gorges Reservoir and explores the mechanisms by which water management and environmental factors affect greenhouse gas emissions. The organic matter in the reservoir mainly originates from phytoplankton and C3 plants, while inorganic carbon is primarily derived from carbonate minerals and soil CO2. Overall, the greenhouse gas fluxes in the reservoir exhibit a “carbon source” characteristic during both the drainage and impoundment periods. The main controlling factors of CO2 and CH4 fluxes in the reservoir vary between different periods. During the drainage period, the main controlling factors of CO2 flux are total phosphorus (TP) and chlorophyll-a (Chl_a), while during the impoundment period, the main controlling factor is total nitrogen (TN). For CH4 flux, the main controlling factor during both the drainage and impoundment periods is dissolved organic carbon (DOC), which is greatly influenced by water management. The different controlling factors are attributed to the changes in environmental factors that affect the biogeochemical processes in the water, thereby influencing greenhouse gas emissions in the reservoir. Therefore, it is necessary to strengthen anthropogenic water management in order to reduce greenhouse gas emissions. However, in the process of strengthening artificial hydrological management, the impact on the water supply network must be considered. By integrating the water network partitioning method used in the water supply network, the management of water reservoirs should also be carried out with a certain degree of partitioning. This can reduce the impact
on domestic water use, hydropower generation from the reservoirs, and other aspects, while reducing carbon emissions, thereby achieving a dynamic balance. This study provides a better understanding of the environmental characteristics and biogeochemical processes in the Three Gorges Reservoir, which can serve as a valuable reference for achieving the goal of “reducing emissions and increasing carbon sequestration” in the reservoir.

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Data Availability Statement: The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

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