Review

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Phytoplankton Blooms in Waterbodies: An Emerging Approach to Greenhouse Gas Mitigation?

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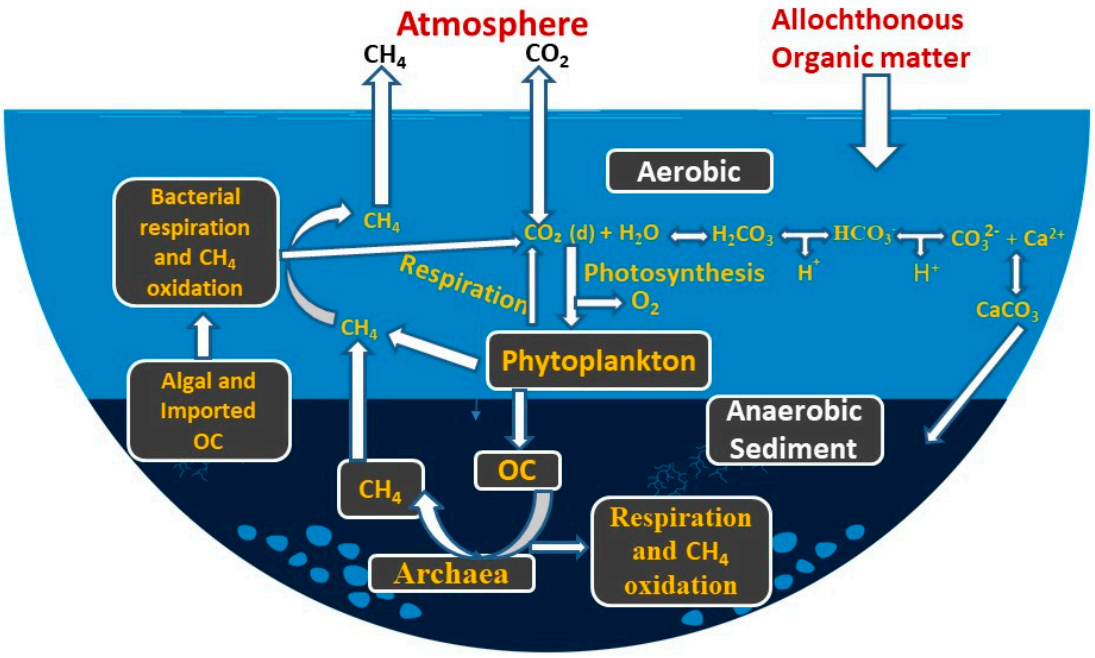
Abstract

A growing body of evidence indicates that freshwater bodies, particularly eutrophic systems, can serve as significant sources of the greenhouse gases (GHGs) carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). In contrast to marine environments, freshwater systems are typically shallower and more directly influenced by terrestrial inputs, including elevated nutrient loading, increased organic matter deposition, and steeper redox gradients in both the water column and sediments. These conditions foster intensive phytoplankton growth and stimulate microbial processes that drive GHG production and emission. This article explores the biogeochemical mechanisms underlying these emissions and assesses the potential of mitigation treatments to harness phytoplankton populations for carbon sequestration and for reducing CH_4 and N_2O release.

Keywords: carbon dioxide; methane; nitrous oxide; greenhouse gases; global warming; eutrophic waterbodies; harmful algal blooms; carbon sequestration; photosynthesis; respiration; sediments



Graphical Abstract

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Conceptual schematic of biogeochemical processes in a eutrophic freshwater body during a phytoplankton bloom. Photosynthesis removes CO_2 and produces O_2, supporting aerobic respiration and methane (CH_4) oxidation in surface waters. Anaerobic sediment layers promote CH_4 production by Archaea using organic carbon (OC), with additional CH_4 potentially formed by phytoplankton in oxic zones. Both external and algal-derived OC are subject to mineralization. Dissolved CO_2 equilibrates with HCO_3^- and CO_3^{2-}, facilitating $CaCO_3$ precipitation in the presence of Ca^{2+}, especially under high pH, with calcite settling to the sediments. CH_4 and CO_2 emissions to the atmosphere are also shown. Local environmental factors govern the magnitude and direction of these fluxes. ***Note:*** Nitrous oxide (N_2O) fluxes are omitted for clarity.

1. Introduction

The rising atmospheric CO_2 concentrations from pre-industrial levels of about 280 ppm to over 420 ppm today, primarily due to fossil fuel combustion and deforestation, and that of other (methane and nitrous oxide) greenhouse gases (GHG) is widely recognized as a major driver of global warming. Along with other GHGs, elevated CO_2 levels contribute to a range of adverse effects, including rising global temperatures, ocean acidification, extreme weather events, and loss of biodiversity, all of which have serious implications for both human and ecological systems. International agreements, such as the Paris Agreement, aim to limit the global temperature increase to well below 2°C above pre-industrial levels. Achieving this target requires not only substantial reductions in ongoing emissions but also active removal of existing GHG from the atmosphere. However, despite global efforts and commitments, the concentration of GHG continues to rise and the trend is accelerating highlighting the urgent need for more effective and immediate action.

Various frameworks have been developed to sequester atmospheric CO_2, broadly classified into two main categories: engineered technologies and nature-based solutions. Engineered approaches such as direct air capture, carbon mineralization, and geological storage typically involve substantial energy requirements, complex infrastructure, and extended development timelines. In contrast, nature-based solutions leverage ecological processes like photosynthesis to remove atmospheric CO_2, generally with lower energy demands and a range of ecological co-benefits. Beyond their role in climate mitigation, biologically driven strategies also support biodiversity conservation, water quality improvement, and ecosystem resilience [1]. Nevertheless, despite the progress achieved through existing initiatives, the total volume of CO_2 sequestered to date remains far below the scale needed to significantly alter the atmospheric carbon trajectory, highlighting the magnitude of the challenge that lies ahead.

1.1. Intensification of Harmful Cyanobacteria Blooms (HCB)

One of the consequences of global warming is the intensification of (HCBs) during the last few decades and their spreading to relatively cold regions where such bloom events were previously unheard of. The blooms capitalize on the elevated dissolved CO_2 concentrations, a rising nutrient supply due to leaching from agricultural fields or poorly treated wastewater and the warming lakes temperatures [2–6] enhancing their photosynthetic activity and enabling them to produce massive, and frequently toxic, biomass [4]. These blooms severely affect the water quality in thousands of waterbodies in both developed and underdeveloped countries and hence the wellbeing of people, wildlife and the biodiversity of infected water bodies. It is estimated that 4.4 billion people currently lack access to clean and toxin-free drinking water worldwide [7].

Another consequence of global warming and HCB is a dramatic decline in the biodiversity of infected waterbodies where toxic cyanobacteria represent over 90% of the photosynthetic organisms. It is widely recognized that, in addition to nutrient availability and various abiotic conditions, both inter- and intra-species interactions, particularly allelopathy, play a significant role in shaping the phytoplankton community composition [8–12]. One example is growth experiments that demonstrated interspecies competition between the dinoflagellate *Peridinium gatunense* and the

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cyanobacterium *Microcystis aeruginosa* which strongly inhibit one another, with the final cell abundance and community composition determined by their initial inoculum ratios and the temperature [13,14]. Since, in most cases, the optimal temperature for dinoflagellate, green algae and diatoms growth is lower than that of toxic cyanobacteria strains, the warming winters plays a major role determining the **seasonal succession** in freshwater systems and in the intensification of HCBs [15]. This is further aggravated by a larger fraction of cyanobacteria cells that overwinter the warmer conditions [16–18] and serve as an inoculum for the HCB population in the spring. The competitive advantage of the larger cyanobacteria population is, in our opinion, one of the main reasons for the HCB intensification over the past five decades.

1.2. Shallow Lakes Are Hotspots for HCB

Shallow eutrophic lakes are more vulnerable to massive phytoplankton blooms compared to deeper lakes. Examples include the (many) lakes in the drainage basin of the Yangtze River in China, Lake Okeechobee in Florida, parts of Lake Victoria in Africa and many others. The main reasons being that the nutrients in the sediments are more accessible to the phytoplankton, closer to the photic zone compared with deeper lakes where they may sink to the hypolimnion and become unavailable for the rest of the summer, due to stratification, awaiting for the forthcoming water mixing in the winter. In shallow water bodies, where the smaller volumes warm up more rapidly in the spring [17], cyanobacteria which thrive in warm conditions gain an early-season advantage, allowing them to establish dominance and outcompete other algae.

Given the strong link between rising atmospheric CO_2 and the growth of HCBs, we examine how mitigation treatments that promote biomass sinking may enhance both organic and inorganic carbon sequestration. We also explore strategies to reduce other GHGs emissions from freshwater bodies, focusing on key processes that govern GHG formation and exchange with the atmosphere. Rather than a comprehensive literature review, we highlight mechanisms affected by algal bloom mitigation, as illustrated in the Graphical Abstract. This approach is especially relevant for eutrophic waterbodies burdened by HCBs, offering a potential pathway to reduce their environmental impact while contributing to climate change mitigation.

2. Sequestration of Organic C

In aquatic systems, organic carbon (**OC**) is produced as part of the **"biological CO_2 pump"** [19–21], whereby **atmospheric CO_2,** dissolved in the sunlit upper layers of the water column, is converted into organic matter through **photosynthesis and associated cellular processes**. In addition to this autochthonous production**, allochthonous organic matter** can also enter the waterbody from the surrounding terrestrial environment. A portion of the OC **descends to the sediments,** contributing to long-term carbon sequestration, while another portion undergoes **microbial decomposition and respiration**, releasing CO_2 and methane (see below) **completing the carbon cycle (Graphical abstract).**

2.1. Are Lakes a Source or a Sink of CO_2?

There are two main sources of CO_2 within the aquatic environment, OC decomposition and calcification (Graphical abstract). Some of the OC produced is buried in the sediment and hence, following thermodynamic principles, lakes should be regarded as a sink for atmospheric CO_2. However, lakes play a complex role in the global carbon cycle, acting as both sources and sinks of CO_2 depending on their location, the season, time of the day and various environmental factors [3,22–25]. Eutrophic lakes emit significantly more greenhouse gases per unit surface area than oligotrophic lakes, though likely less per cell due to self-shading effects on redox conditions. Model-based estimates [22] suggest lakes globally contribute up to 20% of fossil fuel-equivalent CO_2 emissions. While this may seem to contradict the second law of thermodynamics - given that some photosynthetically fixed carbon is buried rather than respired. The key lies in **allochthonous organic**

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carbon input [26–28]. Terrestrial carbon, fixed on land and washed into lakes, is degraded and adds to CO_2 and methane emissions, complicating the system's carbon balance despite signs of in-lake CO_2 drawdown through alkalization and elevated dissolved oxygen (DO) concentration (see below).

2.2. Burial Efficiency (BE) of Organic Carbon

Notably, cyanobacteria produce large quantities and a wide variety of extracellular polysaccharides (EPS), which exert significant influence on their environment, including in biological desert soil crusts, rice paddies, and aquatic systems [29–33]. During intensive blooms, EPS facilitate cell-to-cell adhesion and colony formation, promoting the aggregation of phytoplankton into particulate organic carbon (POC) that sinks toward the sediments as "marine snow" or "flocs." The size of these particles impacts both their sedimentation rate [34] and internal oxygen dynamics; larger flocs exhibit slower oxygen diffusion, potentially leading to anoxic microenvironments within them. Consequently, anaerobic conditions may develop within the flocs delaying biomass degradation by bacterial respiration. In addition, the EPS also affect anaerobic decomposition, condensation of the sediment and mineralization [35,36] by aiding sediment compaction and maintaining structure. Their decomposition produces extracellular organic compounds that inhibits degrading bacterial communities delaying the breakdown of settled cyanobacterial biomass and methane formation, at least in rice fields [37–39].

2.3. Distinguishing Factors in Carbon BE: Lakes vs. Oceans

One of the long-standing dogmas in the field has been that dispersal, grazing by fish and zooplankton and bacterial respiration consumes a large portion of the aggregates, releasing most of the fixed CO_2, while the particles sink to the bottom and during further degradation in the sediments [3,40]. This is indeed the case in the marine environment where only about 1% of the OC produced in the photic zones reach the sediments at >1 km depth [34,41,42] where it remains buried for geological timescale [34,43]. In contrast, detailed studies performed on fresh waterbodies, lakes and reservoirs, spanning various environmental condition, suggested a much larger BE then in the marine environment [26,44,45]. One example is a study performed by the US Geological Survey on 697 waterbodies in continental USA that concluded that the average BE in water reservoirs was 58% [46].

We must conclude that the long-standing dogma that "lakes' OC is much less permanent than in oceans" doesn't withstand empirical evaluation. The results obtained, particularly from eutrophic freshwater bodies show just the opposite. Naturally, the question arises - what distinguishes marine systems from freshwater environments as reflected by the much higher BE in the latter. To clarify this important point, it is essential to reveal the processes driving OC degradation within the waterbody which ultimately determine the OC fraction that reach and then buried in sediments. Briefly, the primary factors influencing these processes are the duration of exposure to oxygen, temperature, and the biomass density.

2.3.1. Exposure to Oxygen and the Temperature

Seminal studies by Sebastian Sobek and colleagues [26,40,45] demonstrated that the BE of POC is strongly influenced by duration of exposure to oxygen during descent to the sediments and by temperature. Prolonged exposure to O_2 and higher temperatures result in lower BE, primarily due to bacterial respiration which consumes OC and nutrients released from lysing cells. Since the oceans are much deeper than lakes the aggregates sinking to the sediments are subjected to grazing and bacterial respiration for a considerably longer duration than in lakes. Further, in shallow lakes, OC particles often reach anaerobic conditions in the sediments within a few meters from the water surface much faster than in the ocean [40,47]. In addition, the massive biomass often observed in eutrophic freshwater lakes, with substantial amount of EPS, forms larger flocs than marine snow. As mentioned, the larger the flocs are the slower is their bacterial degradation.

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Furthermore, the strong currents characteristic of oceanic continental shelves where nutrient inputs fuel intensive algal blooms transport substantial amounts of oxygen to deeper coastal layers, thereby enhancing OC degradation. Ultimately, in addition to the effects of temperature and oxygen [40,41], large spatial variability was observed in the amount of OC reaching specific sediment sites [45] likely reflecting the impact of currents and changing wind directions on local algal abundance. In densely populated waterbodies, the depth of the photic zone (where net oxygen production occurs) is attenuated, particularly in shallow lakes were turbulence by wind or currents may raise sediment particles [48]. Consequently, anoxic condition may develop within a short distance from the water surface [17].

2.3.2. Density of the Phytoplankton Biomass

As indicated, the biomass density is an important parameter affecting the oxygen gradient profile and hence OC degradation. Although blooms intensity increased significantly in the open, oligotrophic, ocean during the last century [49], the overall cell density of phytoplankton biomass is rather low, equivalent to approximately 0.1 - 0.3 mg chlorophyll/m^3. It may reach 5-10 mg chlorophyll/m^3 during spring-summer blooms mostly near coastal nutrient-rich areas. In contrast, the cell density in eutrophic freshwater bodies can easily exceed 300-500 mg chlorophyll/m^3, particularly during HCB that form scums on the water surface [50,51], (https://portal.edirepository.org/nis/mapbrowse?packageid=edi.1756.1). **Chlorophyll extraction methodologies**, along with **recent advances in remote sensing technologies**, have made it easier and more accessible to assess chlorophyll concentrations across large areas. Where evaluations of carbon sequestration are required, conversion factors for estimating dry matter from chlorophyll concentrations [52,53] can be employed. However, **remote sensing** primarily assesses surface phytoplankton populations, while their spatial (including three-dimensional) and temporal distribution is, in most cases, highly variable. Therefore, ground-truthing is essential to accurately calibrate remote sensing measurements. It is timely to develop robust models that integrate remote sensing data with *in situ* measurements to capture the spatial and 3D distribution of phytoplankton, enabling comprehensive, whole-lake assessments. Alternatively, biomass can be estimated by systematically collecting and analyzing samples from multiple locations and depths. However, this method is labor-intensive, costly, and subject to inherent logistical limitations.

2.4. Sequestration of Organic Carbon in the Marine and Freshwater Bodies

Geologically speaking, it is widely recognized that sediments derived from phytoplankton biomass have played a significant role in the formation of kerogen, a key intermediate in the transformation of organic carbon into natural gas and other fossil fuels. This highlights their crucial contribution to the global carbon cycle over geological timescales. For instance, a recent review [54] proposed a model describing cyanobacterial proliferation and the preservation of organic matter, emphasizing their critical role in organic carbon burial throughout Earth's history.

This perspective raises a fundamental question: to what extent can the permanence of OC in a given waterbody be predicted based on its environmental conditions and biological productivity? The concept of **"burial permanence"**- the length of time that OC remains sequestered in sediments is inherently complex as it involves understanding the dynamic processes that govern the **stability and longevity** of OC [55]. **Radiometric dating** of sediment cores using isotopes such as **^{14}C, ^{137}Cs, and ^{210}Pb** is commonly employed to assess the permanence. These analyses provide a detailed reconstruction of the waterbody's depositional history and have been published in numerous peer-reviewed studies [44,56–61], governmental agencies reports (e.g., USGS SIR 2004-5184) and large-scale research initiatives like New Zealand's Lake380 project. Naturally, the preservation **of OC** in the sediment is strongly influenced by **local environmental conditions**. In all cases we are aware of, sediment cores show a pattern of **rapid OC degradation during the first few years,** followed by a **much slower breakdown** phase, highlighting a stabilization process in the deeper sediment layers.

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The reader is encouraged to explore the Lake380 project available on their website and emerging publications thereof. The data represents one of the most extensive and detailed waterbody analyses, over a range of ambient condition, conducted globally. The sediment cores collected as part of this effort offer invaluable data on both **contemporary and historical water quality**, encompassing a broad range of **biotic and abiotic parameters**. In particular, the use of **pigment extraction** and **DNA sequencing** along sediment cores serves as a powerful approach for distinguishing between, and reconstructing of **algal, shrub and trees-originated biomass** over time. Interestingly, the algal originated OC remains fairly constant over tens of thousands of years. This is probably due to various processes taking place in the sediment, where the buried OC undergoes physiochemical processes such as condensation, mineralization, and compaction, ultimately transforming into stable hydrocarbon structures, commonly known as kerogen [37–39,54]. Altogether, offering strong evidence for the capacity of freshwater systems to **sequester OC over long periods.**

2.5. Can Mitigation of Phytoplankton Blooms in Freshwater Bodies Be Used for Substantial Carbon Burial?

Phytoplankton blooms in eutrophic freshwater systems hold promise for **OC sequestration** [62]; however, their **long-term effectiveness and sustainability** remain active areas of research and debate. Under business-as-usual conditions, a substantial portion of bloom-derived carbon is mineralized in the water column (see Graphical abstract), thereby **limiting BE.** In contrast, exposure to **mild but prolonged oxidative stress** has been shown to trigger extensive **programmed cell death (PCD)-like process** in cyanobacteria resulting in cell mortality rates as high as 99% [5,63–66]. This mode of collapse **minimizes the release of cyanotoxins** into surrounding waters [63,67,68].The resulting biomass forms **large aggregates** that **sink rapidly** to the sediment. As reported by Sobek and others [26,40,45], **faster sedimentation rates are strongly correlated with increased BE**. A key working hypothesis is that **PCD-induced massive bloom collapse creates localized anoxia** in bottom waters near the sediment, which in turn inhibits microbial OC degradation via respiration. Over the longer term, **removal of toxic cyanobacteria** enables **phytoplankton succession,** promoting **biodiversity and renewed oxygenic photosynthesis** in the water column even in the face of a dramatic decline in cyanobacterial cell abundance. One additional and noticeable benefit of mitigation-induced bloom collapse is a **marked improvement in water clarity**, enhancing light penetration throughout the water column and thereby photosynthetic oxygen production. Taken together, the BE under these treated conditions may significantly surpass that observed under untreated, baseline scenarios.

Researchers involved in carbon harvesting from phytoplankton blooms may utilize commercial systems that measure **Total Organic Carbon (TOC)** via combustion and CO_2 detection, followed by acidification to quantify **Total Inorganic Carbon (TIC)** enabling full TIC/TOC profiling across depths and locations. **Remote sensing** offers a complementary approach by estimating chlorophyll-a as a proxy for biomass. However, assessing carbon flux to sediments post-mitigation remains challenging due to the **spatial and temporal variability** in HCB biomass, influenced by factors like wind mixing, stratification, light, and nutrients. Addressing this requires an integrated strategy combining **remote sensing, in-situ measurements, and modeling as mentioned in Chapter 2.3.2, above**. While chlorophyll-a accounts for 0.6–1.6% of dry biomass [69] under laboratory conditions, field values may vary. It is recommended that chlorophyll extraction be used to assess its level and carbon content assessed by measuring CO_2 released during combustion.

3. The Fate of Inorganic Carbon in the Marine- and Fresh- Waterbodies

3.1. The CO_2-Concentrating Mechanisms (CCMs)

Cyanobacteria and algae have evolved sophisticated **CCMs th**at enable them to accumulate Dissolved Inorganic Carbon (DIC) within their cells, particularly under CO_2-limiting conditions [70–74]. They can thus be regarded as DIC containing bags, intracellular levels as high as 50 mM DIC were recorded [72]. These mechanisms allow the organisms to elevate the internal CO_2 concentration

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in close proximity to their **carboxylating enzyme, ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco),** which is predominantly localized within **carboxysomes** in cyanobacteria and **pyrenoids** in algae. This adaptation enables them to overcome the large gap between Rubisco's relatively low affinity for CO_2 and the low concentration of dissolved CO_2 in equilibrium with the atmosphere, particularly in cyanobacteria, where the Km(CO_2) of Rubisco is approximately tenfold higher than ambient levels. The size and dynamics of the internal DIC pool are strongly influenced by environmental factors, especially the **CO_2 concentration during growth** and **light intensity**[70,72,75], and they vary among species and even among strains, including *Microcystis sp.* [76,77].

Seminal studies by Elke Dittmann, Martin Hagemann, and colleagues [78–80] revealed a **non-canonical CCM** in toxic *Microcystis sp.*, where a significant part of Rubisco is located outside the carboxysomes. This distribution results in a less efficient CCM compared to the classical model cyanobacteria studied previously. Additionally**, microcystin**, a toxic secondary metabolite produced by *Microcystis* sp., has been shown to bind Rubisco [81]. Fluctuations in extracellular microcystin levels such as those occurring during cell lysis under stress affect the **cytoplasmic localization of Rubisco** [79]. These findings support earlier hypotheses [82] and provide a mechanistic framework for how cells might **sense extracellular microcystin levels** and adjust their physiology to cope with environmental stress, thereby enhancing **ecological fitness.**

A recent study [83] further demonstrated that a similar **non-canonical CCM may also operate in the filamentous cyanobacterium** *Nostoc punctiforme*. Here, a poorly functioning CCM necessitates a reliance on **heterotrophic bacteria** for CO_2 supply under limiting DIC conditions, a surprising dependency that could explain the **difficulty in isolating axenic cultures** of various cyanobacteria and suggests that **elevated ambient CO_2 levels** may be critical for their isolation and cultivation. Finally, a **quantitative analysis of the internal DIC (and calcite) pool** is essential to fully understand the operation and regulation of non-canonical CCMs and their effect on intracellular DIC accumulation [72]. In addition to enhancing the apparent photosynthetic affinity for CO_2, the substantial intracellular accumulation of DIC plays a pivotal role in calcification processes across various algal groups.

3.2. Calcification Processes

The example shown in Figure 1 illustrates that during HCBs, intense photosynthetic activity in the upper layers of the water column, where light is most available, is commonly accompanied by water alkalization. As CO_2 is rapidly drawn down and fixed through photosynthesis, pH levels can exceed 10.0, reflecting a substantial deviation of carbonate chemistry from equilibrium with atmospheric CO_2 (Fig. 1A). Elevated concentrations of dissolved oxygen (DO) in the surface layers (Fig. 1B), exceeding levels expected under equilibrium with air, further support the conclusion that this alkalization is driven by vigorous photosynthetic activity. This alkalization facilitates the precipitation of calcium carbonate, particularly in species with mucilaginous sheaths that promote localized supersaturation, leading to calcite deposition [84–90].

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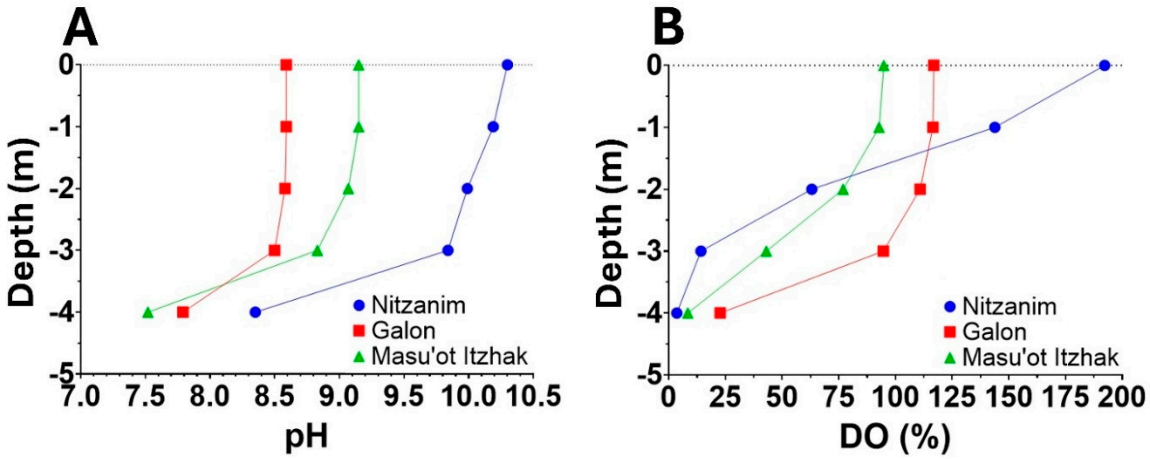

Figure 1. Vertical profiles of pH (A) and dissolved oxygen (DO, B) with water depth in three irrigation reservoirs. Nitzanim and Galon are filled with nutrient-rich, treated recycled water, while Masu'ot Itzhak receives floodwater collected from a nearby stream. Aerial images of the reservoirs (Figure 2A–C) show an extensive bloom in Nitzanim, predominantly *Microcystis* sp., in contrast to Galon (where routine mitigation treatments effectively limit bloom development) and Masu'ot Itzhak where algal growth is constrained by nutrients availability. The pH and DO measurements were performed using a YSI ProDSS Multi-Parameter Water Quality Meter on June 4th , 2025.

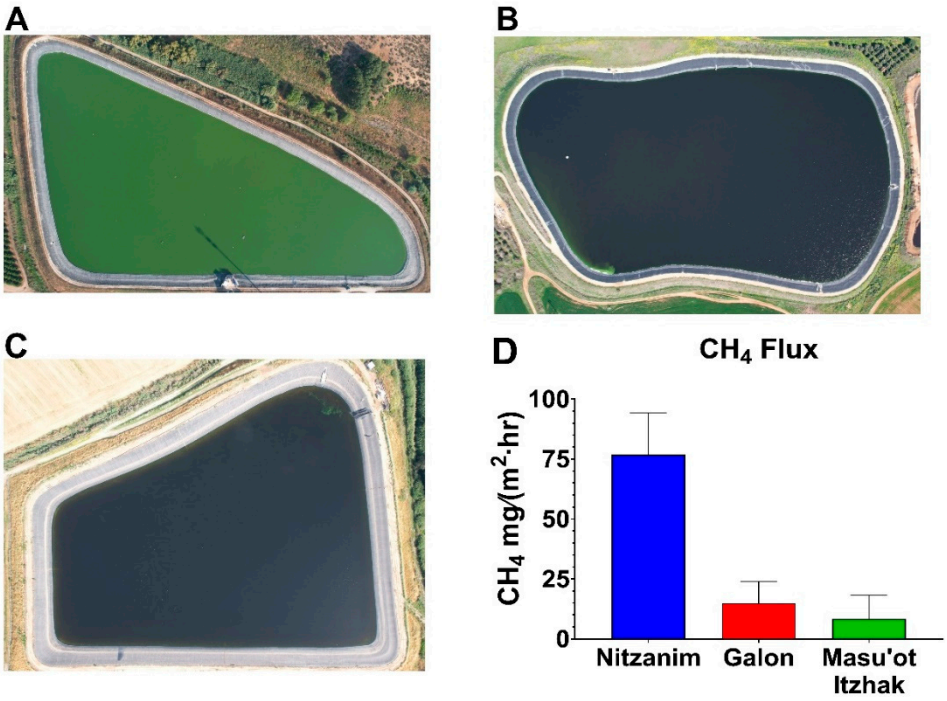

Figure 2. Aerial photographs of the Nitzanim (A), Galon (B), and Masu'ot Itzhak (C) reservoirs, showing the relative phytoplankton (HCB) intensity, along with corresponding methane emission fluxes (D). Methane emissions were quantified using an ABB GLA131 laser-based gas analyzer connected to a custom-built floating flux chamber of known volume and surface area.

$CaCO_3$ accumulation in bloom-forming *Microcystis* sp. has been documented [87,91,92], although quantification of the calcite levels under varying environmental conditions remains incomplete [89,93–98]. Given that cyanobacterial cells can be regarded as DIC-bearing bodies, there

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is potential to employ molecular tools to augment DIC accumulation and, consequently, inorganic carbon sequestration [99,100]. Key targets for such genetic interventions may include bicarbonate transporters (SbtA, BCT1, and BicA), as well as the NDH-1 complexes involved in CO_2 recapture from leaking pools [71,101]. While the environmental release of genetically modified organisms is subject to regulatory constraints, evaluating their capacity for enhanced DIC accumulation and cycling [102] under simulated bloom conditions could provide valuable insights into their potential for carbon capture applications.

Calcification in aquatic systems involves the reaction of Ca^{2+} with HCO_3^- to form calcium carbonate ($CaCO_3$), releasing CO_2 (and water, Graphical abstract). This process can lead to CO_2 emissions from both freshwater and marine environments [89,90,96,103,104]. However, the accumulation of calcium carbonate in sediments suggests a net uptake of DIC over time, as atmospheric CO_2 dissolves in water to replenish bicarbonate consumed during calcification. In freshwater bodies, significant calcification often occurs in areas with high alkalinity, hard water or during substantial phytoplankton blooms. Intensive CO_2 uptake during phytoplankton blooms raises the pH to values where most of the inorganic carbon is in the form of carbonate, promoting calcite precipitation [105]. The Sea of Galilee (Lake Kinneret), a stratified *hard-water* lake, provides a notable example. It was estimated that over 52,000 tons of calcite settles into the sediment during the spring blooms of the dinoflagellate *Peridinium gatunense* [93,106]. Mineralization processes within the sediment also lead to carbonate formation particularly during intensive algal blooms [107]. Here, calcification is driven by the high level of dissolved CO_2 consequent on intensive bacterial respiration. It is estimated that carbonate formation through mineralization at the sediment accounts for 3–8% of the deposited OC. However, distinguishing this carbonate from that settling onto the sediments from the top water layer remains challenging [35]. Attempts to resolve this issue using $\delta^{13}C$ would be complicated by the disequilibrium between CO_2 and bicarbonate species at both the sediment surface and in the photic zone. This disequilibrium, driven by a substantial pH gradient, significantly shifts the $\delta^{13}C$ values of these species away from the equilibrium value of approximately 7‰ [108].

Naturally, the amount of carbon buried through calcification is strongly influenced by various factors, with calcium, magnesium and proton concentrations playing a particularly significant role. These concentrations vary widely between different lakes and depth in the water column (Fig. 1A) and affects both calcification and dissolution processes. Unfortunately, detailed analyses of the amount of carbonate reaching the sediments, whether due to calcification in the epilimnion or mineralization of OC, and its subsequent fate, including the extent of dissolution [104], remain scarce. Direct measurements of descending carbonates using sediment traps and cores provide valuable insights, though these techniques are labor intensive and costly with substantial variation observed among replicates. Alternatively, an assessment of calcium and magnesium cycles within the waterbody through measurements of their levels in the epilimnion, hypolimnion, as well as inflowing and outgoing streams throughout the year offers a robust approach to evaluate calcification and dissolution dynamics. In the case of Lake Kinneret, analysis [109] revealed that approximately one-third of the calcite formed during the spring bloom undergoes dissolution, while the remaining portion remains buried (Nishri, personal communication). Such assessments are crucial for evaluating carbon fluxes in aquatic environments, understanding their role in the global carbon cycle, and exploring potential pathways for effective carbon sequestration.

A Challenge: Can We Use Changing pH to Assess the Amount of Atmospheric CO_2 Dissolution?

The extent of pH rise during intensive CO_2 consumption by photosynthesis (Fig. 1A) is strongly influenced by the alkalinity of the waterbody and the chemical nature of its buffering components. Higher alkalinity results in a smaller pH increase for a given amount of CO_2 withdrawn. In principle, alkalinity can be used to estimate the amount of CO_2 required to reverse the pH across a given range, such as restoring pre-bloom conditions, assuming equilibrium among DIC species during the process. However, this equilibrium-based assumption can be misleading. Unlike oceanic systems, eutrophic lakes often exhibit significant disequilibrium among DIC species, driven by dynamic

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biological and chemical processes, most notably the intensive removal of CO_2 during photosynthesis and the precipitation of carbonates at elevated pH. The latter process is especially pronounced when calcium and magnesium ions are sufficiently available leading to effective removal of DIC from the water column and further complicating efforts to model or quantify DIC speciation accurately. To address this complexity, we propose a time-resolved modeling approach based on observed pH dynamics, incorporating non-equilibrium processes that may provide a more accurate framework to estimate CO_2 fluxes.

When a harmful cyanobacterial bloom (HCB) is abruptly terminated—for example, through mitigation treatment—the cessation of photosynthetic CO_2 uptake permits dissolved CO_2 in the water to re-equilibrate with the atmosphere, typically resulting in a gradual decline in pH toward pre-bloom levels. The rate of atmospheric CO_2 dissolution (E) is influenced by abiotic factors such as temperature, wind, turbulence, and vertical mixing. Additional contributors to the rising CO_2 concentration include respiratory CO_2 production (B), the absence of photosynthetic uptake (C), and shifts in the distribution of dissolved inorganic carbon (DIC) species as the system rebalances with changing pH (D).The relationships between these fluxes can be described as:

$$A = (B - C) + D + E$$

where (A) is the amount of CO_2 required to reduce the pH over a given range

A key challenge is whether we can quantitatively distinguish between the contributions of each of these processes, in order to extract the net amount of CO_2 dissolved from the atmosphere following bloom collapse. Potential approaches include measuring the initial rate of pH decline in sealed water samples (excluding air exchange) may provide insight into non-atmospheric CO_2 contributions (e.g., from respiration and internal redistribution). Early time points are critical since prolonged incubation can result in substantial pH reduction by microbial respiration alone, especially if oxygen and organic carbon are available. A more robust method involves quantifying DIC directly by acidifying collected samples, which converts all carbonate species to CO_2 for measurement. This bypasses the reliance on pH-alkalinity modeling alone. We acknowledge that spatial heterogeneity, both horizontal and vertical, and temporal fluctuations in pH and alkalinity (see Fig. 1A) are inherent to the dynamics of bloom development and collapse. These variations are also reflected in local dissolved oxygen levels (Fig. 1B), which integrate the combined effects of photosynthesis, respiration, and gas exchange with the atmosphere. To account for these variabilities, representative sampling across depth profiles, followed by volumetric integration over the entire waterbody, is recommended.

4. The Methane Enigma

The escalating methane (CH_4) level in the atmosphere is a matter of growing concern due to its projected impact on global warming, surpassing CO_2 (per mol) by approximately 30-fold. It is now firmly established that waterbodies constitute significant contributors to atmospheric methane [110–118]. Large spatial and temporal variations in methane emissions were revealed. Using Eddy covariance approach over small waterbodies Hounshell and colleuges [119] and Waldo et. al. [120] showed that under a business-as-usual conditions eutrophic lakes release 1.3-51.4 g CH_4 m^{-2} yr^{-1}, respectively. Unfortunately, this methodology that measures the vertical fluxes of gases (such as CO_2 and CH_4) and monitors fluctuations in wind speed and directions above the ecosystem (aquatic or terrestrial), is currently applicable to small waterbodies only. One of the challenges is to capture methane that dissolves in the water-column where a significant portion can escape via ebullition directly into the atmosphere. Buoyant flow chambers enables measurement of the methane emission using its infrared absorption bands or gas chromatography [121].

4.1. Methane Biosynthesis

The mechanisms of methane biosynthesis and degradation are being resolved with recent findings challenging longstanding paradigms and potentially unveiling new strategies to mitigate CH_4 emissions. Biogenic CH_4 is primarily produced under anaerobic conditions by several archaea

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groups known as methanogens. They can combine CO_2 and hydrogen to form methane in a reaction that consumes the OC produced within the lake, as well as from allochthonous inputs from its surroundings. Additional important methane producing pathways include methylotrophic bacteria that can convert methanol to methane and CH_4 production by phytoplankton under oxic condition (discussed below). In addition to O_2 level, methane formation is also affected by temperature though in some case less than expected since presence of various methanogens whose optimal activities vary across a wide temperature range.

Biogenic methane has the lowest isotopic carbon ratio compared to other natural sources because it is extremely depleted in ^{13}C [122]. Its **$\delta^{13}C$ value,** typically ranges from **-50‰ to -110‰** (relative to the Vienna Pee Dee Belemnite standard, VPDB), is the main diagnostic tool that distinguish it from other methane sources. This highly depleted isotopic signature is due to the preferential use of the lighter carbon isotope (**^{12}C**) by methanogenic archaea during microbial methanogenesis, particularly in the reduction of CO_2 or acetate to methane via the two main pathways involved. However, studies utilizing methane to assess the efficacy of CH_4-derived carbon as a substrate for phytoplankton [123,124] should bear in mind that ^{13}C discrimination also occurs during CO_2 fixation, and that the CO_2-concentrating mechanism in phytoplankton raises the utilization of ^{13}C by the carboxylating enzyme [72].

The Methane Paradox

Until recently, the prevailing belief was that under business-as-usual conditions, most CH_4 produced in anoxic sediments is consumed by methanotrophs in the overlying oxic layers. This paradigm was supported by laboratory experiments and studies in small-scale aquatic systems, but recent research challenges this view. A growing body of evidence indicates that various phytoplankton inhabiting the photic, oxygenated water layers, including cyanobacteria, can produce significant amounts of CH_4 during photosynthesis [112,125–133]. This aligns with earlier studies on aerobic CH_4 biosynthesis by bacteria [134].

Collectively, these findings contribute to the recognition of the "methane paradox," wherein CH_4 concentrations in the oxic surface layers of lakes and coastal ocean regions rise toward the top water layer and can surpass levels expected at saturation with air [124,132,135]. The specific organisms involved in freshwater and oceanic methane production are being identified [131,135,136], and the exact metabolic pathways are under intensive investigation. Recent studies have demonstrated that CH_4 formation is light- and photosynthesis-dependent, though the precise mechanisms remain poorly understood [131]. It is hereby hypothesized that CH_4 production may serve as a safety valve to release excess reducing equivalents in the photosynthetic machinery during high illumination or other stress conditions.

Stable carbon and hydrogen isotope analyses suggest that methylated compounds such as methylphosphonate (MP), methylamine, and methionine serve as precursors for oxic CH_4 production. This process involves a gene cluster (phn) that is widespread in filamentous cyanobacteria and also present in certain strains of toxic *Microcystis* sp., such as those collected during a large bloom in Dianchi Lake, China [137], emphasizing the role of cyanobacteria in oxic methane formation. Complicating matters further, studies suggest that MP released by lysing cyanobacteria is utilized by bacteria as a phosphate source, thereby releasing CH_4 in the photic zone [137]. Mutations in the C–P lyase phosphonate degradation pathway of the marine bacterium *Pseudomonas stutzeri* disabled its ability to produce methane [135]. Currently, accurate assessments of the relative contributions of cyanobacteria and eukaryotes to methane formation and utilization in the upper aerobic zone are lacking, highlighting the need for genome screenings and identification of potentially involved genes [130].

4.2. Methane Consumption

Methane is consumed by methanotrophic microorganisms, which utilize it as both a carbon and a reducing power source, thereby mitigating its emission to the atmosphere. The activation of the

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stable C–H bond in methane is thermodynamically unfavorable, requiring a high redox potential and the transfer of eight electrons [138].

Methane oxidation proceeds via two main pathways: aerobic and anaerobic. These pathways differ significantly in their enzymatic mechanisms, the organisms involved, and their sensitivity to environmental factors such as temperature and redox potential. In both systems, methane is oxidized by forms of methane monooxygenase (MMO) or analogous enzymes, each exhibiting distinct kinetic properties. In aerobic methanotrophs, MMOs utilize molecular oxygen as the terminal oxidant. In anaerobic methanotrophs, however, the enzymes rely on alternative oxidants such as Fe^{3+} or copper. In anoxic aquatic environments, particularly in marine systems, sulfate or nitrate can serve as terminal electron acceptors for methanotrophic respiration. These enable energy production that indirectly supports methane oxidation under oxygen-depleted conditions, thereby contributing to CH_4 removal even in anoxic zones.

As mentioned, the eight-electron transfer involved in aerobic methane oxidation is mediated by specific components of the MMO enzyme complex, which catalyzes the conversion of CH_4 to methanol, a key step in the metabolism of methane by aerobic methanotrophs. In anaerobic methane oxidation, CH_4 is ultimately converted to CO_2 and water through the action of microbial consortia, typically involving anaerobic methanotrophic archaea in partnership with sulfate-reducing bacteria. Where sulfate availability is limited, such as in freshwater lakes, alternative electron acceptors like nitrate, iron or manganese can be utilized.

Theoretically, an oxidation-reduction potential (ORP) above approximately +400 mV is likely required to support meaningful anaerobic methanotrophic activity. For reference, the redox potentials of key electron acceptors used in anaerobic processes, Fe^{3+}/Fe^{2+} and NO_3^-/NO_2^- are +770 mV and +940 mV, respectively. It is important to note that in most aquatic systems studied to date, nitrate is often depleted in the oxic (photic) zone but remains abundant in deeper, anoxic layers of the water column. Therefore, measuring the redox potential at the sediment-water interface is recommended to assess the potential for anaerobic CH_4 consumption and of the impact of iron fertilization on anaerobic methane oxidation. In contrast, the redox potential required for aerobic CH_4 oxidation is provided directly by oxygen, acting as the terminal electron acceptor during bacterial respiration. Thus, where possible, simultaneous measurements of ORP and dissolved oxygen are highly recommended to better understand the methanotrophic potential and to evaluate strategies for enhancing methane removal in aquatic systems.

As previously noted, cyanobacteria are increasingly recognized as significant contributors to CH_4 production. However, despite CH_4 being a potential source of both carbon and reducing power and despite cyanobacteria's capacity to support eight electron transfer processes such as nitrogen fixation, they appear to lack the MMO enzyme necessary for cleaving the stable C–H bond in methane. To date, no published studies have demonstrated the growth of axenic cyanobacterial cultures using CH_4 as the sole carbon source. Nevertheless, growing interest in cyanobacteria–methanotroph interactions has led to co-culture studies that reveal enhanced CH_4 oxidation in the presence of cyanobacteria. This enhancement is likely attributable to increased local oxygen availability provided by cyanobacterial photosynthesis. Conversely, methanotroph presence has been associated with accelerated cyanobacterial growth [123,139]. The exact metabolic contribution of methanotrophs to cyanobacterial physiology remains unclear. Given the highly efficient CCMs in cyanobacteria, it is unlikely that these benefits are due solely to respiratory CO_2 release by methanotrophs, as previously proposed.

In the absence of extensive data from freshwater systems, insights may be drawn from studies on cyanobacteria–methanotroph interactions in rice paddy soil microcosms. In such systems, inoculation with cyanobacteria has been shown to reduce CH_4 emissions by up to 90%, with outcomes strongly dependent on the cyanobacterial species used. For instance, *Nostoc sp.* and *Calothrix sp.* were found to influence different methanotrophic communities, leading to variable outcomes in methane flux [37].

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These emerging studies point to a more complex and nuanced picture of methane dynamics within microbial consortia, highlighting the potential role of species-specific interactions and even secondary metabolites in mediating these effects. Continued exploration of these relationships is essential for understanding their ecological significance and potential applications in methane mitigation strategies.

4.3. Can HCB Mitigation Reduce Methane Emissions?

Naturally, the net flux of CH_4 emissions from waterbodies is governed by the balance between its production and consumption. The significant variability observed in CH_4 emission fluxes across different eutrophic lakes likely reflects differences in local conditions and various parameters affecting this balance. Studies have shown that cyanobacterial blooms can enhance methane emissions through multiple pathways. For instance, research on Lake Tai, China, showed that regions with dense cyanobacterial populations emitted significantly more CH_4 compared to low-density areas, 867 vs. 3.4 μg CH_4 m^{-2} min^{-1}, respectively indicating a strong correlation between bloom intensity and methane production [139]. This is an important observation, as it may point to a potential route for decreasing global methane emissions from eutrophic lakes through proper management and control of HCBs.

Three water reservoirs located in the northwestern Negev region of Israel were selected to examine this possibility - Nitzanim (5 ha, Fig. 2A) and Galon (6 ha, Fig. 2B) are filled with tertiary treated recycled nutrient-rich water, whereas Masu'ot Itzhak (8 ha, Fig. 2C) is supplied with water collected from occasional winter floods in a nearby stream. Aerial photographs taken by drone clearly show a dense phytoplankton population in Nitzanim, while phytoplankton presence is barely visible in Galon and Masu'ot Itzhak. Routinely mitigation treatment applied in Galon Reservoir effectively suppressed the HCB that are typically observed in Nitzanim. This difference is further supported by the higher surface pH (Fig. 1A) and dissolved oxygen (DO) concentrations (Figure 1B) in Nitzanim, likely resulting from intensive photosynthetic activity associated with the denser HCB population. Additionally, the steeper vertical decline in both pH and DO in Nitzanim suggests stronger light attenuation, and thus reduced oxygen production at depth, caused by the bloom's density.

Measurements of methane flux (Fig. 2D) revealed substantially higher CH_4 emissions in Nitzanim compared to the other two reservoirs. It remains to be determined whether the lower emissions observed in Galon and Masu'ot Itzhak are primarily due to reduced CH_4 production by cyanobacteria or to a lower availability of organic carbon in the sediments, which serves as a substrate for methanogenesis. Nevertheless, these preliminary findings are encouraging and underscore the need for further research to elucidate how local environmental factors shape the balance between methane production and consumption, ultimately influencing net emissions. Further, the emerging correlation between eutrophic conditions, bloom intensity, and methane release suggests that bloom-targeted mitigation strategies, such as those employed in Galon Reservoir, may offer an effective approach to reduce CH_4 emissions from eutrophic waterbodies.

5. Nitrous Oxide in Freshwater Bodies

In addition to its detrimental effects on the ozone layer, nitrous oxide (N_2O) is a potent greenhouse gas (GHG), with a global warming potential approximately 270 times greater than that of CO_2. In recent years, freshwater lakes have been recognized as significant sources of atmospheric N_2O emissions [22,140–142]. Cyanobacteria and microalgae have been implicated in N_2O biosynthesis in aquatic environments [143–146].

The primary contributors to N_2O production in waterbodies are microbial processes, particularly ammonia oxidation and denitrification. In oxic waters, ammonia-oxidizing Archaea and Bacteria release N_2O as a byproduct during the oxidation of ammonia to nitrite. Under oxygen-depleted conditions, N_2O also serves as a key intermediate in the denitrification pathway, in which nitrate and nitrite are sequentially reduced to molecular nitrogen (N_2), often coupled with the oxidation of organic matter.

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Phytoplankton blooms can significantly influence N_2O dynamics by altering the structure and extent of oxic–anoxic transition zones (Fig. 2D), such as at the sediment–water interface or within stratified water columns. These zones are critical sites for microbial nitrogen transformations, and shifts in redox gradients can determine whether the dominant end-product of nitrogen metabolism is benign N_2 or climate-active N_2O.

Despite its environmental significance, mechanistic understanding of N_2O synthesis and degradation in aquatic systems is poorly understood. Recent research is unfolding the complex interplay of biotic and abiotic pathways that govern N_2O fluxes [147]. Gaining a deeper understanding of these mechanisms is essential for improving nitrogen cycle models in eutrophic waterbodies and developing strategies to mitigate N_2O emissions from inland waters. Interestingly, recent studies have shown that sunlight can drive abiotic N_2O production in both freshwater and marine systems. This occurs primarily through photochemical reduction of nitrate to nitrite, followed by subsequent reactions leading to N_2O formation [148]. However, the precise mechanisms and global relevance of this pathway are still under investigation.

Of note, some methanotrophs are capable of anaerobic methane oxidation using nitrate or nitrite as electron acceptors, effectively reducing one GHG (CH_4) while potentially producing another, far more harmful (N_2O) through a synergistic metabolic process. As with methane, it remains to be determined whether mitigation treatments targeting algal blooms which can significantly reduce organic matter and alter redox dynamics will also lead to measurable reductions in N_2O emissions to the atmosphere.

6. Concluding Remarks

The intensification of **HCBs** in eutrophic lakes, primarily driven by **anthropogenic nutrient enrichment and global warming** has been linked to **increased GHG emissions**, thereby contributing to **global warming.** While **mitigation strategies** targeting HCBs hold considerable promise for substantial **reduction of these emissions**, a better understanding of the **mechanisms involved** and **environmental factors** that regulate them is critical. Advancing such knowledge will not only enhance the **effectiveness of current mitigation efforts** but also support the development of **targeted, science-based approaches** for minimizing global GHG emissions across a variety of aquatic ecosystems.

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