

Review

Greenhouse Gases Emissions of Constructed Wetlands: Mechanisms and Affecting Factors

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Abstract: Constructed wetlands (CWs) widely applied for wastewater treatment release significant greenhouse gases (GHGs), contributing to global warming. It is essential to characterize the comprehensive source-sink effects and affecting factors of GHGs in CWs, offering references and guidance for designing and operating CWs to better control GHG emissions. However, current reviews focus on individual GHG emission mechanisms. With the aid of the Web of Science Core Collection database, the relevant literature on carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) emissions in CWs after 2010 was collected and organized. As highlighted in the review, CWs can produce and transmit these GHGs into the atmosphere, forming sources of GHGs and sequestration CO₂ through plants photosynthesis, forming sinks of GHGs. Their overall performance depends on many factors. Hybrid CWs, *Cyperus papyrus*, *Cyperus alternifolius*, and *Iris pseudacorus*, adsorption substrates like Fe-C, low temperatures, and a C/N ratio of five are beneficial for GHG mitigation in CWs. Future studies should focus on in-depth research into the mechanisms and overall source-sink benefits of plants and microorganisms in relation to GHGs. This review provided a comprehensive understanding of the emission mechanisms and affecting factors of the major GHGs in CWs, bridging the research gap in this field, helping researchers to clarify the context, and providing valuable in-sights for further scientific investigations.

Keywords: greenhouse gases; constructed wetlands; source and sink; mechanisms; affecting factors



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1. Introduction

Global climate change is one of the most critical challenges facing humanity today [1], largely driven by greenhouse gas (GHG) emissions [2], profoundly impacting both Earth's ecosystems and human society's sustainability [3]. Among the numerous GHGs, carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) are the most extensively studied due to their significant emissions and potent greenhouse effects, with a 70%, 23%, and 7% contribution to the greenhouse effects, respectively [4–6]. CO₂, mainly from burning fossil fuels [7], has the most serious and significant global warming effect due to its huge and far greater total emissions than other GHGs. CH₄ is the second most abundant GHG after CO₂, and its warming potential is 25 times larger than CO₂ over a 100-year time horizon [8]. A 1-fold increase in atmospheric CH₄ concentration was reported to result in 0.2–0.3 degrees of surface warming in the tropospheric, posing serious risks to human

and environmental health [9]. However, the lifetime of CH_4 is only about 10 years, so its emission reduction can realize the purpose of restraining rapid global warming in a short time [10]. Although N_2O is emitted less in CWs, the greenhouse effect of N_2O is 296 times larger relative to CO_2 over a 100-year time horizon, and its remaining time in the atmosphere is 120 years [11]. Even a small increase in N_2O emissions may make a non-negligible contribution to global warming. Since industrialization, human activities have significantly increased the emissions of GHGs [12]. The Intergovernmental Panel on Climate Change (IPCC) (one of the important international organizations established to address climate change) has highlighted that the levels of GHGs in the air continue to rise, and the world is warming faster than ever in at least the last two thousand years [13–16].

For years, efforts to mitigate GHG emissions have been ongoing worldwide. Within China, research efforts have focused on measuring and monitoring GHG emissions in various industries, leading to the establishment of national GHG inventories and emission baselines [17–19]. Chinese government policies have promoted clean energy development, energy conservation, and the establishment of a carbon trading market, incentivizing emission reduction [20–27]. Internationally, considerable progress has been made in the development and application of carbon capture and storage (CCS) technologies [28–30]. Advanced models and methodologies have been developed to estimate GHG emissions and their potential impacts [31–34]. Additionally, studies on the carbon cycles of ecosystems, such as forests, wetlands, and oceans, have been conducted to understand their roles in GHG balance [35–38]. Global cooperation has fostered data sharing and collaborative transnational projects [39–41].

Unexpectedly, in these efforts, constructed wetlands (CWs), seemingly beneficial for various wastewater treatment [42–48], cost-effectively, have emerged as an unsuspected source of GHG emissions, warranting attention [49–53]. A literature analysis of 158 papers from 1994 to 2013 showed that the median values of CO_2 , CH_4 , and N_2O emission flux in CWs are $95.8\sim137.0\text{ mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, $3.0\sim6.4\text{ mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, and $0.09\sim0.13\text{ mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, respectively [54]. Lishan Tan et al. [55] proposed that CWs significantly increased the CH_4 emissions compared to those of natural wetlands. In addition, several studies indicated that in terms of unit sewage, the total GHG emissions of surface flow CWs and horizontal subsurface flow CWs are significantly higher than that of most activated sludge processes [56–58].

In order to mitigate the consequences of global warming, controlling GHG emissions has become one of the urgent tasks of mankind. The Paris Climate Agreement proposed to pursue efforts to limit global warming to less than 1.5 degrees C above pre-industrial levels by the end of this century [59]. Considering the rapid spread of CWs worldwide, evaluating the source-sink effects of GHGs presented by the system is essential. However, there is still a research gap in the comprehensive review of the source-sink effects, emission mechanisms, and affecting factors of the three major GHGs in CWs. This paper aims to fill this gap by collecting and reviewing relevant literature on GHG emissions in CWs over the past decade. Based on the literature review, the paper systematically provided an overview of the types, structures, and water purification mechanisms of CWs, organized and summarized the source-sink effects, emission mechanisms, and affecting factors of CO_2 , CH_4 , and N_2O in CWs, and presented future research prospects.

2. CWs and Their Source-Sink Effects on GHGs

2.1. Overview of CWs

CWs are nature-like systems that combine vegetation (emergent, floating, or submerged), substrates (rocks, soils, synthetic materials, among others), and microbial communities [60,61], achieving water purification using the joint action of plant uptake, microbial activity, and substrate adsorption under controlled environment [62]. According to design structures and flow direction, CWs are divided into three major groups, as represented in Figure 1. Free water surface flow constructed wetlands (FWS CWs); horizontal subsurface flow constructed wetlands (HSSF CWs); vertical subsurface flow constructed wetlands

(VSSF CWs) [63]. Hybrid-constructed wetlands (HCWs) systems combine these three kinds of CWs differently, aiming to achieve a higher treatment [64].

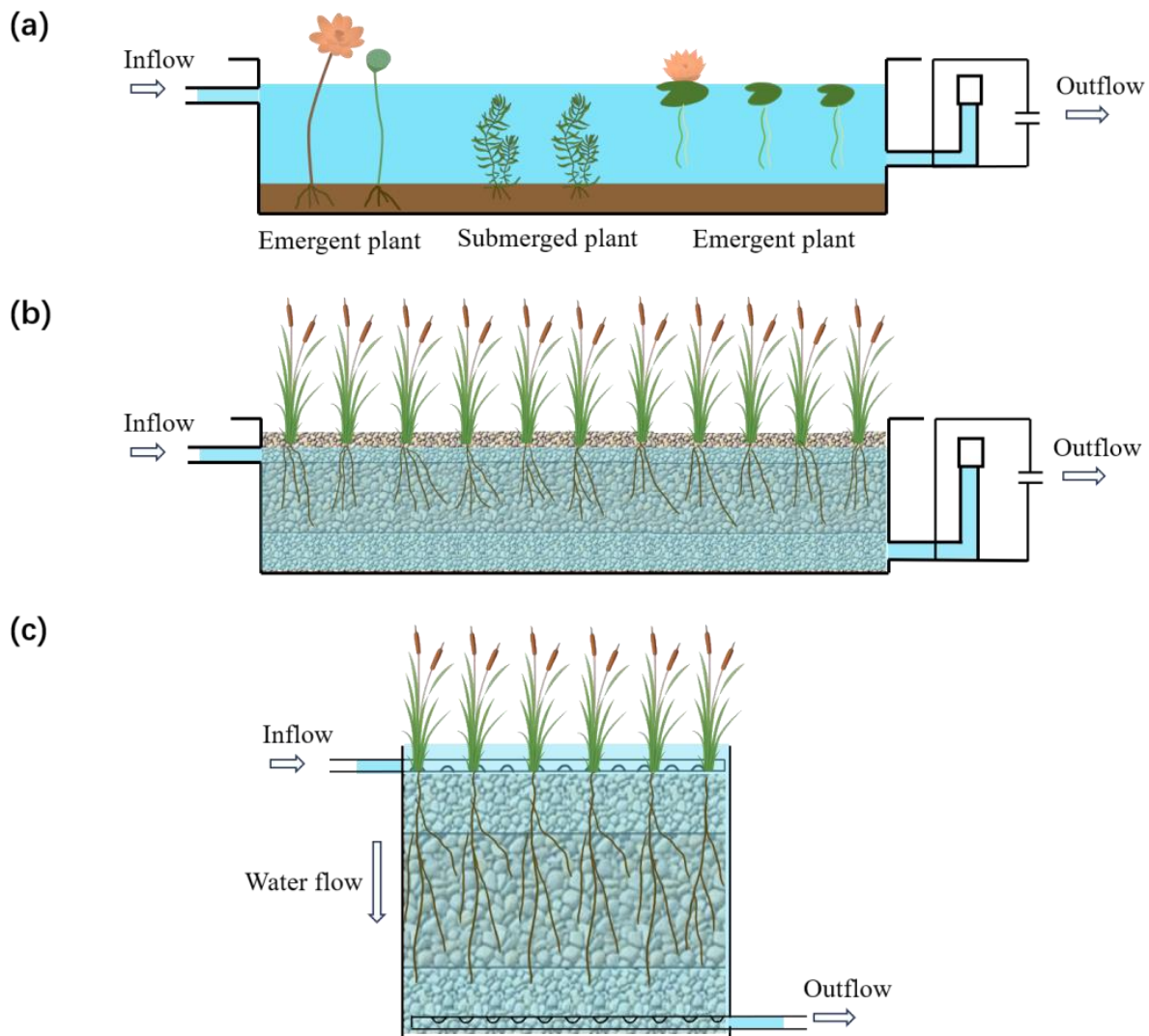


Figure 1. Constructed wetland configurations: (a) A free water surface flow constructed wetland with three types of plants; (b) Planted horizontal subsurface flow constructed wetland with *Typha orientalis*; (c) Planted vertical subsurface flow constructed wetland with *Typha orientalis*.

2.1.1. Free Water Surface Flow Constructed Wetlands (FWS CWs)

FWS CWs are shallow water-filled basins typically containing 20–30 cm of rooting soil. They feature open water areas with a 20–40 cm depth, often with over 50% of the surface covered by floating, submerged, and/or emergent plants [63]. The FWS CWs operate most similarly to a natural wetland [65], where water flows in a push stream with a low reoxygenation rate, making most of the area in the filler anaerobic [66]. In this type of CW, plants are not usually harvested, and their litter can provide essential organic carbon for denitrification [67]. Suspended solids are efficiently eliminated through the combined processes of settling and filtration facilitated using the dense vegetation [68]. Nitrogen is primarily eliminated through nitrification (in the water column) and subsequent denitrification (in the litter layer), along with ammonia volatilization triggered by algal photosynthesis, particularly under higher pH levels [63].

2.1.2. Horizontal Subsurface Flow Constructed Wetlands (HSSF CWs)

HSSF CWs are composed of gravel or rock beds, typically with a depth of 0.6–0.8 m, to facilitate plant root growth. These beds are planted with emergent macrophytes such as *Phragmites australis*, *Calamus*, *Cattails*, *Scallions*, etc. [69], and sealed with an impermeable layer to prevent seepage and ensure regulated outflow [70]. The wastewater enters through the inlet and moves slowly through the porous medium beneath the bed's surface, following a horizontal path to the outlet. It is collected at the outlet and controlled before being discharged through a water level control structure [71]. In these systems, plants and rhizosphere microorganisms form a symbiotic relationship. Plants provide organic matter and oxygen to microorganisms through root exudations and oxygen release [72]. In return, rhizosphere microorganisms expand the absorption range of plant roots by establishing connections with plants, providing them with water and minerals that are challenging to obtain, and protecting plants against weed space competition and certain diseases [73]. Anoxic/anaerobic processes play a crucial role in HSSF CWs due to the permanent saturation of the bed [74]. Suspended solids are retained mainly by filtration and sedimentation [75]. Organic compounds are primarily removed via microbial degradation under anoxic/anaerobic conditions [76]. Denitrification is the main pathway for nitrogen removal, while ammonia removal is limited by oxygen availability in the filtration bed [63].

2.1.3. Vertical Subsurface Flow Constructed Wetlands (VSSF CWs)

VSSF CWs typically comprise a graded gravel bed ($\varnothing$ approximately 30–60 mm) overlaid with sand ($\varnothing$ approximately 6 mm) and are planted with the same species of emergent macrophytes as HSSF CWs [77]. In contrast to HSSF CWs, this type of CW is intermittently fed with a substantial volume of wastewater, resulting in surface flooding. The water then slowly infiltrates the bed and is gathered using a drainage network at the bottom until the bed is completely emptied, facilitating air replenishment [78]. This feeding method increases the oxygen transfer rate and has a strong reoxygenation capacity, leaving the bed mostly aerobic and, therefore, providing suitable conditions for nitrification but not for denitrification, resulting in high nitrate effluent [79]. VSSF CWs are also very effective in removing organics and suspended solids [80]. Regarding sewage treatment per population equivalent (PE), VSSF CWs require less land than HSSF CWs [54]. Moreover, both VSSF and HSSF CWs equipped with bed insulation capacity can function in colder climates compared to FWS CWs [54].

2.2. CWs' Source-Sink Effects on GHGs

The role of CWs in global climate change is complex due to their potential to act as both a source and sink of GHGs. In the CW system, plants convert atmospheric CO₂ into organic matter through photosynthesis and fix it in the sediment [81]. Although some of this can be quickly recycled into the atmosphere via respiration, much is also incorporated into the organic carbon of the sediment via microbial assimilation, filler absorption, and plant action like plant litter accumulation [54]. The anaerobic environment in the sediment makes the organic matter lack oxidation conditions and slows the decomposition rate [82]. This organic carbon accretion in sediment makes CWs a greenhouse gas sink [83]. The combination of elevated water tables, high productivity, and lower decomposition has led to significant carbon storage in sediment, especially in high-latitude wetlands [84]. CWs are a source of GHGs via releasing CH₄ and N₂O from wastewater and sediment into the atmosphere [55]. The predominantly anaerobic and N-rich environment is particularly favorable for the methanogens (specialized anaerobic archaea) and nitrogen-cycling bacteria production of these two gases [49]. There is no consensus on whether CWs are the source or sink of GHGs. Some studies have shown that most CWs are sinks of CO₂ equivalents (CO₂ (eq)) [77]. In this case, the CO₂ (eq) plant biomass immobilization overcomes the GHG emissions, showing a sink effect [77,85]. On the contrary, some studies have shown that most CWs are sinks of CO₂ and sources of CH₄ and N₂O [38,55], but they show a source effect of GHGs in general since the warming potential of CH₄ and N₂O are much

greater than that of CO_2 [86]. Brix et al. [87] proved that because of the different infrared absorption characteristics and atmospheric longevity of CH_4 and CO_2 , *Phragmites australis* wetlands may be regarded as a source for GHGs on a short time scale (<60 years), but as a sink for GHGs if evaluated over longer time scales (>100 years) [88]. Whether CWs are a source or sink of GHGs is affected by several factors, including CW type and age, plant presence and species, substrate type, environmental conditions, feeding strategy, etc. [77,84]. For example, Wu et al. [89] found that the planted CW was a net CO_2 sink, while the unplanted CW was a net CO_2 source. These factors indirectly affect carbon sequestration and GHG emissions by influencing microbial activities [90]. Multiple factors work together in the complex system of CWs to determine their impact on GHG emissions and carbon sequestration. Therefore, understanding the mechanisms and affecting factors of GHG emissions in CWs is vital for increasing CWs' role as sinks and decreasing their role as sources of GHGs.

3. GHG emissions Mechanisms of CWs

3.1. Emission of CH_4 and CO_2 in CWs

Both CO_2 and CH_4 are carbon-based GHGs, which are produced by the metabolism and transformation of organic matter mainly from wastewater, substrate (soil), plant biomass, litter, dead wood, and root exudates formed via plant fixation of CO_2 in CWs systems [91,92]. CO_2 , the most critical GHG, is influenced by the combined functions of plants and soils in controlling their atmospheric concentration. During photosynthesis, plants assimilate atmospheric CO_2 and convert it into sugars and other carbon compounds. These carbon compounds are subsequently transferred to the soil through root exudates, litter, etc. Later, through the respiration of plants, microorganisms, and soil animals, as well as the chemical oxidation of carbon-containing substances, CO_2 is generated and released back into the atmosphere [93]. The CO_2 emitted in the process of biological cycling from the carbon absorbed by plants of CWs during photosynthesis is of biogenic origin; this part was generally not included in national total emissions [94,95]. The net emission of CH_4 is determined by its production, transport, and oxidation processes [96], as shown in Figure 2.

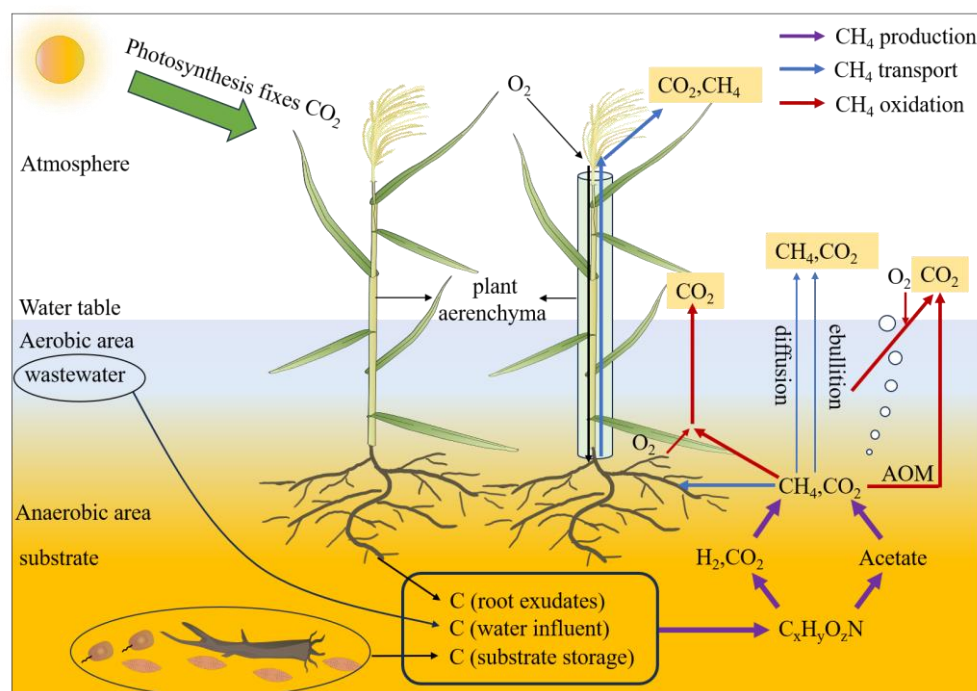


Figure 2. Production, transport, and oxidation processes of CH_4 in CWs.

3.1.1. Production of CH₄ in CWs

The emission of CH₄ from CWs to the atmosphere depends on the balance of activities of methanogen and methanotrophs [97]. Recently, different mechanisms of methane production and oxidation have been discovered.

According to the classical methane-producing mechanism, under anaerobic conditions, anaerobic hydrolytic microbes, fermentative microbes, and hydrogen-producing acetogens can decompose organic matter into simple inorganic (e.g., CO₂ and H₂) and organic compounds (e.g., acetate) that are subsequently converted to CH₄ via methanogens [98]. Methanogenic archaea are the earliest prokaryotic microorganisms of life on Earth and the major contributors to global atmospheric methane emissions [99]. The methanogens found so far belong to Euryarchaeota, which consists of 7 orders, namely *Methanopyrales*, *Methanococcales*, *Methanobacteriales*, *Methanomicrobiales*, *Methanosarcinales*, *Methanocellales* and *Methanoplasmatales*/*Methanomassiliicoccales* [100–102]. Methanogens have a narrow trophic range, primarily utilizing a small set of simple substrates, including H₂ + CO₂, acetate, formate, methylated compounds (such as methanol, methylamines, and dimethyl-sulfur), as well as primary and secondary alcohols [103]. As a result, these archaea often work with bacteria, which degrade complex organic matter into small molecules in an anaerobic environment that are then used by methanogenic archaea to produce CH₄. Based on the type of small molecule substrate utilized, archaeal methanogenesis can be categorized into three well-known metabolic pathways: H₂/CO₂ reduction, acetic acid fermentation, and methyl compound cracking [104]. Studies have indicated that the hydrogenotrophic pathway is energetically more advantageous for methanogenesis compared to the acetoclastic pathway [105]. In contrast, the dominance of the acetoclastic pathway has been observed in freshwater wetland ecosystems, contributing to over 67% of CH₄ emissions [106]. Additionally, a new study published in Nature suggested that the archaeon '*Candidatus Methanoliparum*' alone can combine the degradation of long-chain alkanes with methanogenesis without the help of bacteria, and this alkylotrophic methanogen may have a crucial role in the transformation of hydrocarbons into methane [107].

Well into the 21st century, people have realized biogenic methane formation is far more complicated than this story. Methanogenic archaea are not the only ones that can produce methane, and the reaction conditions are not limited to anaerobic environments. In a new study in Nature journal, a team led by the University of Heidelberg in Germany has developed a subversive idea. All living cells possess a common mechanism of CH₄ formation that is based on interactions among reactive oxygen species (ROS), iron, and methyl donors, opening new perspectives for understanding biochemical CH₄ formation and cycling. This reaction does not require enzymes, and the process is not complicated, as shown in Figure 3. First, ROS reacts with ferric ions to produce highly reductive hydroxyl radicals ($\cdot\text{OH}$), which then react with a methyl donor to form a methyl radical ($\cdot\text{CH}_3$), and finally, the methyl radical combines with the hydrogen radical ($\cdot\text{H}$) to produce methane molecules. The contribution of this reaction to CH₄ emissions remains uncertain. Factors such as heightened metabolism, elevated temperatures, introduction of external reactive oxygen species, and inflammatory responses can amplify the production of CH₄ through this mechanism [108]. Certain terrestrial plants that produce CH₄ have been utilized in CW applications, including *Phragmites australis* and *Thalia dealbata*. Plants have been reported to produce CH₄ to defense against environmental stress factors, including cutting damage, elevated temperatures, UV radiation, and disruption of cytochrome c oxidase activity [109]. When plants initiate stress responses, excessive production of ROS, such as H₂O₂, can occur within plant cells, intensifying the breakdown of cellular components and ultimately resulting in CH₄ production [110]. Nevertheless, investigating CH₄ emissions from hydrophytic plants in CWs under aerobic conditions remains unexplored, indicating a critical knowledge gap that necessitates further research [104].

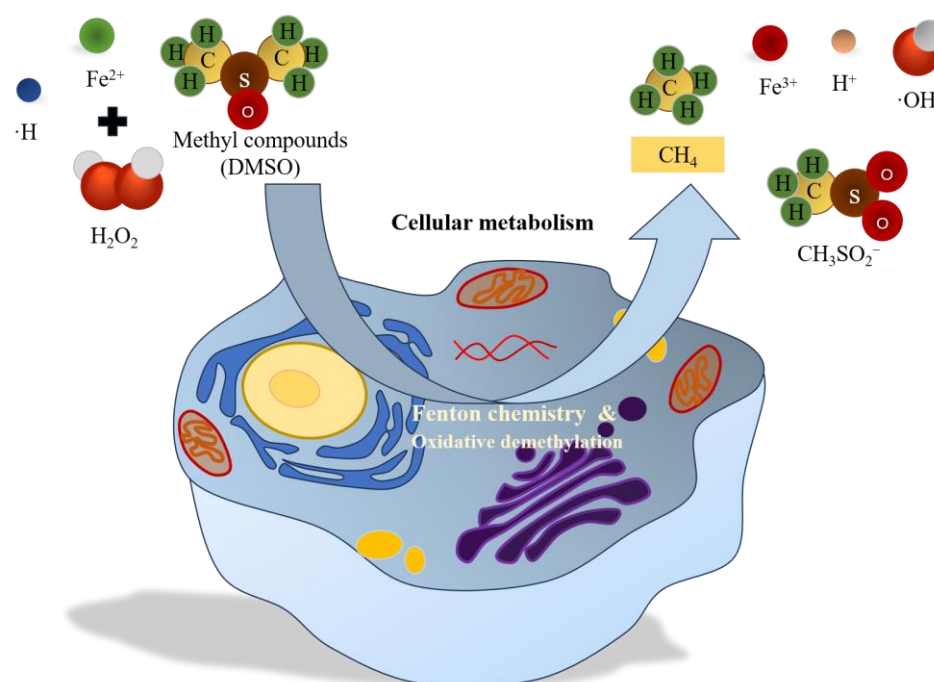


Figure 3. Aerobic methane oxidation in all living cells is based on the reference [108].

3.1.2. Transport of CH₄ in CWs

Methane produced in CWs is transported in three main ways: molecular diffusion from the water and substrate column, ebullition flux process from the substrate column, and plant-mediated CH₄ transport from the substrate column via plant aerenchyma [111], among which the third is the primary way of CH₄ release, accounting for about 70% of the total-CH₄ emissions [112]. Ebullition produces three-fold more CH₄ fluxes than molecular diffusion [113]. Plant-mediated CH₄ transport mechanisms can be categorized into molecular diffusion or convective transport processes, where oxygen is transported to the roots. At the same time, gaseous microbial by-products are released from the plant roots into the atmosphere [114]. Generally, convective transport processes exhibit incredible speed than molecular diffusion processes [115].

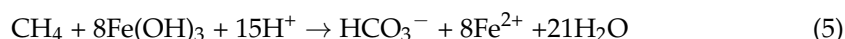
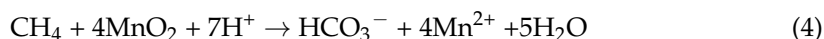
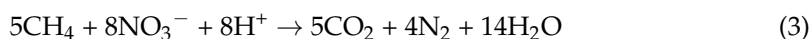
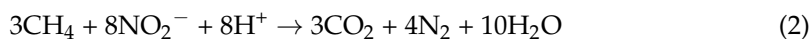
3.1.3. Oxidation of CH₄ in CWs

During the CH₄ transport process, it can be oxidized through aerobic or anaerobic pathways, an important factor affecting the CH₄ flux in CWs.

The aerobic oxidation of CH₄ conducted by bacteria called methanotrophs primarily occurs at micro interfaces where CH₄ and O₂ coexist, such as substrate-air interface, water-air interface, the rhizosphere, and internal tissues of plants [113], with rapid reaction rates, depending on the concentration of O₂ [116]. The aerobic oxidation of CH₄ is widely recognized as the primary CH₄ sink within the wetland system, effectively oxidizing over 50% of the CH₄ generated in CWs [117].

Anaerobic oxidation of methane (AOM) is a process for anaerobic oxidation of methane via microbes using electron acceptors other than oxygen, such as sulfate (sulfate-reduction-dependent anaerobic methane oxidation, SAMO), NO₂⁻/NO₃⁻ (nitrite-dependent anaerobic methane oxidation), metal oxides (e.g., Fe₃⁺ and Mn₄⁺ anaerobic methane oxidation, metal-AOM), and direct interspecies electron transfer [118,119]. The above AOM reaction can be expressed by the following chemical Equations (1)–(5). In addition, Valenzuela et al. used isotope experiments to show that CH₄ anaerobic oxidizing bacteria can also couple the reduction in natural organic humus in 2017 [120]. Some studies believe that AOM is a

neglected CH₄ sink. Guerrero-Cruz et al. found that AOM can reduce CH₄ emission by more than 50% in a study on freshwater wetlands [119].



Most of the CH₄ produced in CWs is oxidized to CO₂. Brix et al. investigated the annual carbon flux of *Phragmites*-dominated wetlands in Denmark and found that the annual fixed CO₂ of the CW was 98 mol/m². Of this, 17 mol/m² is converted to CH₄, while 76% of them is oxidized to CO₂, and only 4 mol/m² is finally discharged from the CW system [87], as shown in Figure 4. The abundance, composition, and activity of methanogens and methanotrophs are essential determinants of methane emissions [121]. Options to reduce CH₄ emissions mainly rely on reducing CH₄ production and promoting CH₄ oxidation [54]. It is affected by CW type, plant species, substrate type, O₂ supply, available carbon source, salinity, etc. Methyl coenzyme M reductase (mcrA) and particulate methane monooxygenase (pmoA) are critical enzymes in CH₄ production and oxidation, resulting in their use as phylogenetic biomarkers for methanogens and methanotrophs [122].

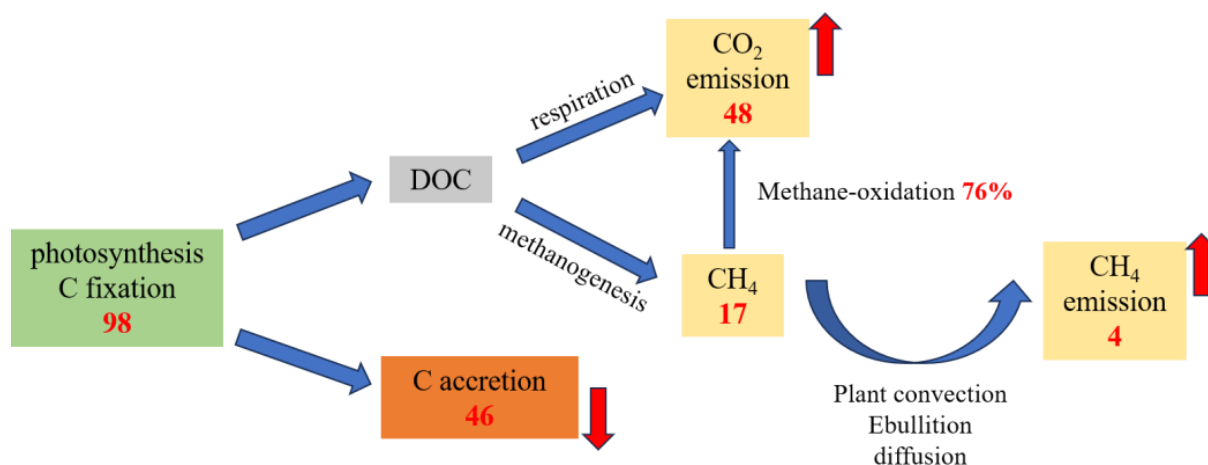


Figure 4. Summary of estimated rates of carbon cycling in the *Phragmites australis* wetland at Vejlerne Nature Reserve, Denmark, based on the reference [87]. The red narrows denote where the carbon ends up. Figures denote the estimated annual rates of the processes indicated (unit: mol C m^{−2} year^{−1}).

3.2. Emission of N₂O in CWs

Most studies have suggested that N₂O in the CW system is formed in the process of nitrifying and denitrification via microorganisms, as shown in Figure 5. Inorganic autotrophic microorganisms perform the complete nitrification process and consist of two processes. The first process is the oxidation of ammonia nitrogen to nitrite via ammonia-oxidizing bacteria (AOB). The catalytic enzymes of this process include ammonia monooxygenase (Amo) and hydroxylamine oxidoreductase (Hao) [123]. The second process is the oxidation of nitrite to nitrate via nitrite-oxidizing bacteria (NOB). The key enzyme of this process

is nitrite oxidoreductase enzyme (Nor). In the first process, NH_4^+ is oxidized to NH_2OH by Amo, then NH_2OH is catalyzed by Hao and generates nitroxyl (HNO) as an intermediate. HNO reacts with another NH_2OH molecule, then dimerizes into hyponitrous acid ($\text{H}_2\text{N}_2\text{O}_2$), and finally chemically decomposes to form N_2O [124]. N_2O can also be generated through a bio-abiotic coupling process involving the interaction of HNO_2 and NH_2OH [125]. Hence, the N_2O generated from AOB nitrification becomes particularly significant during the shift from aerobic to anaerobic conditions and should not be disregarded [126]. Denitrification is a continuous process ($\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$) in which denitrifiers reduce NO_3^- to N_2 under low oxygen or anaerobic conditions, and N_2O is produced as a conventional intermediate product [127]. The catalytic enzymes of this process include nitrate reductase (Nar), nitrite reductase (Nir), nitric oxide reductase (Nor), and nitrous oxide reductase (Nos). The production of N_2O in the denitrification process can be attributed to two possible reasons. Firstly, the activity of Nos is influenced by factors such as dissolved oxygen, pH, carbon source, and toxic substances, leading to the accumulation of N_2O [128–130]. Secondly, certain denitrifiers like *Pseudomonas fluorescens* lack Nos, causing N_2O to be the final product of their denitrification reaction [131].

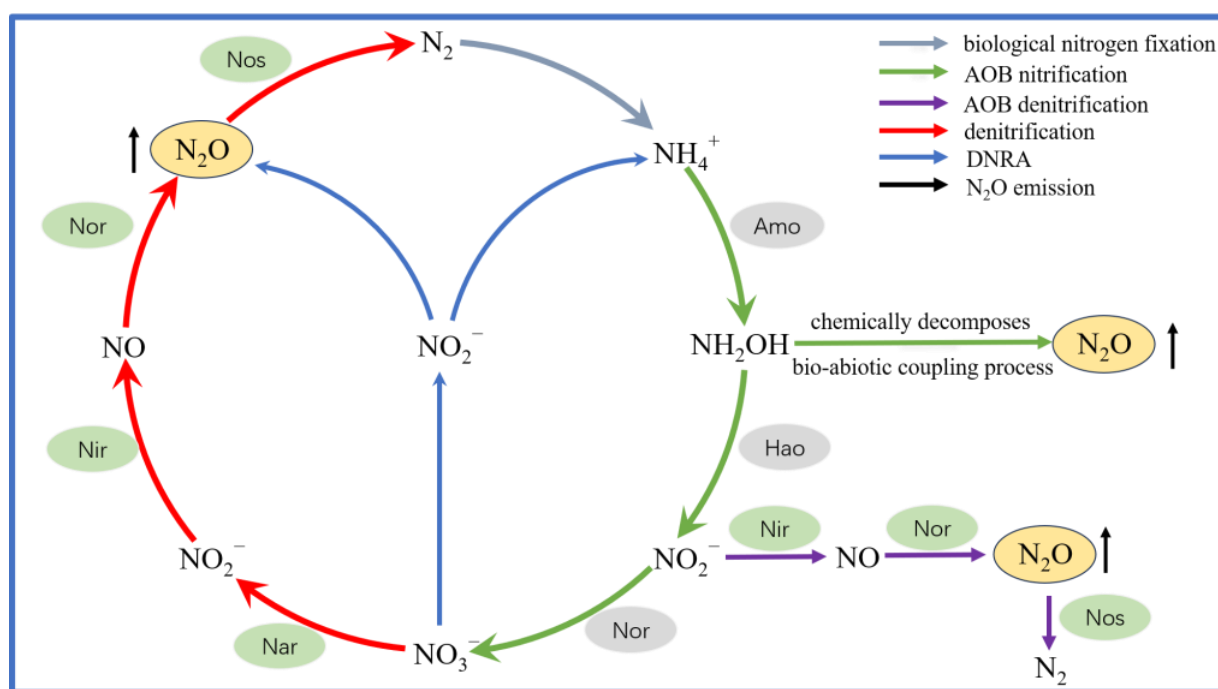


Figure 5. The mechanisms of N_2O production.

CWs are a chimera of aerobic, anaerobic, and anoxic microbial sites. In addition to the traditional nitrification and denitrification, a variety of advanced N-removal processes also occur here, including dissimilatory nitrate reduction to ammonium (DNRA), simultaneous nitrification-denitrification (SND), denitrification by nitrifiers, denitrification by aerobic denitrifiers, etc. In recent years, more and more studies have focused on the production of N_2O in these advanced N-removal processes. DNRA involves the transformation of nitrate into bioavailable ammonium salts in anaerobic environments, accompanied by the production of N_2O . This process typically occurs in a low redox potential environment. The unique structure of CWS results in extensive anaerobic zones within their interior, providing favorable conditions for DNRA [132]. The amount of N_2O produced by SND is less than that produced by sequential nitrification and denitrification, and the amount of N_2O is also influenced by the concentration of dissolved oxygen and the amount of carbon source [133]. Denitrification by nitrifiers is incomplete nitrification; that is, nitrifiers oxidize ammonia to nitrite and then use nitrite as an electron acceptor to generate N_2O ,

NO, and N₂ ($\text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$). Studies have shown that this reaction tends to occur in high nitrogen, low carbon, low oxygen, and low pH environments [134]. In the nitrification system, in addition to nitrifier denitrification, aerobic denitrifiers may also be another reason for the reduction in nitrite under aerobic conditions to produce N₂O. The end product of some aerobic denitrifiers was reported only as N₂O [135]. The amount of N₂O produced by denitrifiers in aerobic conditions exceeds that generated in anoxic conditions, likely due to oxygen's inhibition of N₂O reductase. The extent of aerobic denitrifiers' contribution to N₂O production remains uncertain.

The main pathway of N₂O production still needs to be clarified. Some studies suggest that the process of N₂O produced by NH₂OH oxidation is minimal, whether it is a chemical or biological reaction [136]. Li et al. further reported that denitrification is the main reason for stimulating N₂O emission [137]. In comparison, Chen et al. indicated that the aerobic stage in most wastewater treatment systems is the primary source of N₂O production [138].

Nitrous oxide produced in CWs is transmitted to the atmosphere through diffusion, ebullition, and plant ventilation. Plants can also fix nitrogen in the air through nitrogen-fixing bacteria, thus providing a source of N₂O [139].

4. Affecting Factors of GHG Emissions in CWs

4.1. Type and Age of CWs

The differences in GHG emissions among different types of CWs can be attributed to variations in their internal dissolved oxygen (DO) levels and redox potential, which are determined by their structure (water table position) and feeding strategy. Most studies have indicated that the CH₄ emissions from subsurface flow CWs are significantly lower than those from FWS CWs, and within subsurface flow CWs, the emissions are lower in VSSF CWs compared to HSSF CWs [140,141]. This is because VSSF CWs have a suitable aerobic/anaerobic interface due to intermittent flooding, which is beneficial for both aerobic methane oxidation and AOM processes [142]. FWS CWs are mainly in an anoxic state, and HSSF CWs have anoxic-anaerobic conditions, showing negative Eh level (−100 mV to 500 mV) and low dissolved oxygen (DO) concentration (<2 mg/L) [143], which facilitates the anaerobic production of CH₄ [77]. Furthermore, in subsurface flow CWs, where the water table is below the substrate surface, CH₄ emissions are reduced as the produced CH₄ undergoes oxidation during its movement through the water layer via diffusion and ebullition [113]. In surface flow CWs with a high water table, CH₄ emissions are increased as they enter plant root systems in the deeper anaerobic layer and are transported to the atmosphere through the aerenchyma [144]. However, the aerobic/anaerobic interface intensified the activity of N₂O during nitrification and the activity of nitrous oxide reductase during denitrification, which intensified the production of N₂O and inhibited the further reduction of N₂O to N₂, resulting in the accumulation of N₂O. Thus, the N₂O emission of VSSF was generally higher than that of FWS CWs [145]. According to Liu et al., the FWS CW exhibited the highest CH₄ emission rate (36.6 mg·m^{−2}·d^{−1}) and the lowest N₂O flux (0.1 mg·m^{−2}·d^{−1}). In contrast, the VSSF CW showed the lowest CH₄ emissions but the highest N₂O flux (2.2 mg·m^{−2}·d^{−1}). The combined VF-SF-FWS constructed wetlands demonstrated relatively efficient nitrogen and phosphorus removal and had a lower global warming potential than any single wetland type [146,147]. Several reports have highlighted hybrid CWs' advantages in terms of both water purification and reduction in GHG emissions [54,148]. There are few long-term research papers on the effect of CW age on GHG emissions. A study showed that CO₂ and CH₄ increase with the age of operation of CWs within 10 years, probably due to the accumulation of organic matter, while N₂O emissions remain unchanged, and the average temperature increases by 3 °C after 10 years of operation [149]. At the same time, most studies suggest that over longer timescales (>100 years), CWs act as a sink of GHGs [87,88].

4.2. Plant

Plants play many vital roles in CWs, not only influencing microbial processes and their by-products via the release of oxygen and available carbon from plant roots to the soil but also acting as a significant transport channel for GHG emissions into the atmosphere. In addition, plants fix CO₂ from the atmosphere into sediments via photosynthesis. Therefore, the effect of plants on GHG emissions in CWs is complex, which can either increase or decrease GHG release [54], depending on the presence, species, richness, growth situation, harvest of plants, etc.

The effects of plant presence on GHG emissions from CWs could be more consistent. Some studies have shown that the low molecular weight organic matter exudated via plant roots provides substrate and energy for microbial activities and promotes the production of GHGs [54,150]. It is suggested that CO₂ fluxes are higher in planted CWs than unplanted CWs. The number of AOB bacteria around the roots of planted CWs is greater than that of unplanted CWs, thus increasing the release of N₂O, and N₂O emissions increase with plant species richness [151]. The presence of vascular plants was reported to lead to significantly higher total respiration rates than un-vegetated control plots [152]. However, some studies indicated that the organic matter exudated by plants provides sufficient carbon sources for the denitrification process, which reduces the release of N₂O [153]. The plant rhizosphere's aerobic environment stimulates methanotroph growth, which is conducive to the oxidation of CH₄ [154]. Planted CWs mainly acted as the carbon sink (about 13,000 mg·m⁻²·d⁻¹ net CO₂ absorption flux) and could cover the emission of N₂O and CH₄ (maximum 12.24 mg·m⁻²·d⁻¹ and 2.52 mg·m⁻²·d⁻¹, respectively) [155].

The impact of plant diversity on GHG emissions is also controversial. Several studies have observed a positive correlation between CH₄ emissions and plant species diversity [156], as high species diversity increases carbon source availability and promotes CH₄ emissions [109]. In contrast, some studies have also found that plant species diversity has no significant influence on CH₄ emissions [157]. Additionally, research indicates that plant diversity can enhance carbon sequestration within the substrate, effectively offsetting the global warming potential associated with CH₄ and N₂O emissions. This phenomenon also promotes the transformation of CWs from carbon sources to carbon sinks [156].

In conclusion, this variation is potentially due to plant species variation. Different plant species show different GHG productivity. Some plants provide aerenchyma to transport O₂ to the plant rhizosphere, promoting methane oxidation in the micro-oxygen environment, such as *Cyperus papyrus* and *Cyperus alternifolius* [53,140]. In contrast, certain plant species, such as *Juncus effusus*, possess remarkable abilities to transport GHGs. They can directly transport CH₄, generated within anaerobic environments, to the atmosphere, bypassing the aerobic soil layer and increasing methane emission [144,158]. In addition, some plants have a strong carbon sequestration ability and could cover the emission of nitrous oxide and methane, acting as the carbon sink, such as *Iris pseudacorus* [155].

During the growing season, microorganisms preferentially utilize the small molecular organic matter secreted by the plant roots, while the plant's lignified rhizome biomass is deposited in the substrate as refractory carbon during other times of the year [159]. It has been observed that plants tend to promote the release of CH₄ and N₂O during the growing period, and the release of CH₄ and N₂O decreases after stem wilt [143], while studies have also shown that the CH₄ produced by plant litter entering wetland systems accounts for 40% of the total release, which is an important reason for the increase in GHG emissions [160]. Upon harvesting the plant, the CH₄ stored in the plant root system is rapidly released, and the plant stems are directly exposed to the air, leading to an immediate increase in CH₄ release [161].

4.3. Substrate

The role of traditional substrates in CWs is mainly to adsorb pollutants and support microbes and plants [97], including soil, sand, gravel, ceramsite, etc. Among them, soil and fine sand exhibit a higher water retention capacity, limiting oxygen transmission

to the system and resulting in an anaerobic environment, which increases the amount of CH₄ released [162]. Recently, some novel substrate amendment schemes have been applied in CWs to improve the treatment efficiency of CWs. Carbon-rich substrates like biochar [53,94] promote CH₄ production, but they also stimulate plant roots to secrete more oxygen, enhancing methane oxidation [163]. The overall impact of biochar on CH₄ emissions is still uncertain, emphasizing the necessity for additional research to elucidate the role of biochar in regulating CH₄ emissions [164]. Electron-exchange substrates, such as Mn ore and iron ore substrates, can directly inhibit the activity of methanogens and promote the AOM process under the influence of dissimilated metal-reducing bacteria, resulting in a reduction in CH₄ emissions [165,166]. Moreover, the toxicity of Fe³⁺ affects the N₂O reductase activity so that N₂O cannot be converted to N₂, increasing N₂O release [167]. Adsorption substrate types, such as Fe-C [168], can not only increase methane and oxygen adsorption via activated carbon [169,170] but also compete with methanogens for substrate in the presence of iron-reducing bacteria, ultimately reducing CH₄ emissions [171]. Zhang et al. reported that the presence of biochar and hematite mitigated CH₄ and N₂O emissions by modifying microbial communities with higher ratios of *pmoA*/*mcrA* and *nosZ* genes abundances, as well as increasing the abundance of denitrifying bacteria (*Dechloromona*, *Thauera*, and *Azospira*) [172]. The research of Huo et al. suggested that the biochar-CWs and pyrite-CWs provided carbon source and electron donor, respectively, which directly intensified the heterotrophic denitrification process in CWs and then reduced the emission of N₂O. In pyrite-CWs, adding Fe (II) as an electron donor might directly mediate the occurrence of autotrophic denitrification and reduce the emission of N₂O [173].

4.4. Temperature

Temperature affects GHG emissions in CWs by influencing microbial activity and the succession of dominant bacteria. Methanogens are very sensitive to temperature changes [174], with the optimal temperature for methanogenesis usually 35 °C–40 °C [175], and the diversity and abundance of methanogens will increase with the rise of temperature [176], resulting in a significant increase in the rate of CH₄ production. Higher summer temperatures can improve methanogens' activity and increase CH₄ emissions because rapid oxygen consumption affects the activity capacity of methanotrophs [177]. Low temperature will reduce the rate of organic matter degradation, thus weakening the activity of methanogens and fermenting bacteria [38], thus reducing the substrate utilization of methanogenesis. Methanotrophs are not sensitive to temperature, and the optimal temperature is 25 °C. CH₄ can be oxidized either at low to −2 °C or at high to 30 °C [178]. Research generally indicates that CWs release higher amounts of CH₄ during the warm seasons than cold seasons [98,179,180]. According to Lu et al., methanogens were dominated by *Methanosarcinaceae* (utilizing acetate and H₂/CO₂ substrates), while as temperature lower, *Methanosaetaceae* (using acetate for CH₄ production) dominated the methanogens [181]. Significantly higher N₂O emission during the summer than during winter due to a slow-down of the denitrification and nitrification processes at lower temperatures was found by Ström et al. [182]. There are also some findings showing that temperature is not positively correlated with GHGs because other factors besides temperature collectively affect the total emissions of GHGs [183–185].

4.5. Influent Characteristics

Influent characteristics also affect GHG emissions, including influent organic carbon load, NH₄⁺, NO₂[−], NO₃[−], TN load, and C/N. A high C load will increase the supply of organic substrates for methanogens, and a high influent organic load will lead to rapid oxygen consumption and reduce the oxidation of CH₄, thus increasing CH₄ emissions. When nitrifiers oxidize NH₄⁺, they compete with methanotrophs oxidizing CH₄ for the active site on methane monooxygenase (MMO), and CH₄ oxidation could not begin until NH₄⁺ was consumed [186]. Higher concentrations of NH₄⁺ can inhibit the growth and activity of methanotrophs by increasing the number of nitrifiers, thus inhibiting CH₄ oxi-

dation [186]. Furthermore, the presence of NO_2^- , NO_3^- , and cations in conjunction with NO_3^- resulting from NH_4^+ oxidation can directly hinder the activity of methanotrophs, leading to the inhibition of CH_4 oxidation [187,188]. In contrast, increasing NO_3^- concentrations stimulate organic matter decomposition, resulting in elevated CO_2 emissions and reduced CH_4 emissions via anaerobic CH_4 oxidation [189–191]. A high TN load reduces DO during nitrification, causing NO_2^- accumulation. This, coupled with the faster reaction rate of AOB compared to NOB, triggers N_2O production via NH_4OH oxidation and nitrifier denitrification [192]. Several studies reported an optimal C/N ratio of around 5 for simultaneously best biological nutrient removal and lowest CO_2 and CH_4 fluxes [193,194]. Wu et al. [195] found that when C/N = 5, the nitrogen removal effect of sewage is the best, and the release of N_2O is the least, while when C/N < 4~5, the denitrification reaction is incomplete, resulting in the accumulation of NO_2^- . Accumulated NO_2^- will inhibit N_2O reductase activity, increasing N_2O release [193]. In addition, due to the weak electron competition ability of N_2O reductase, N_2O accumulation is easy to occur when the carbon source is insufficient [169]. However, higher C/N is sometimes better; High C/N may also increase N_2O release. For example, studies have shown that when the C/N ratio is 20, the release of N_2O is 10 times that when the C/N ratio is 5. This may be due to the excessive influent organic load leading to the system pH being too low (<5), thus inhibiting the N_2O reductase [195].

In conclusion, the GHG emissions in CWs are influenced by multiple factors. Crucial influencers encompass CWs type and age, plant presence, diversity, species, growth stages, substrate types, temperature, and influent characteristics. CW type significantly impacts GHG emissions due to variations in DO levels and redox environments. The presence and diversity of plants can either stimulate or suppress GHG release, with specific plant species and growth stages showing stronger connections to GHG emissions. Novel substrate types like biochar, electron-exchange substrates, and adsorption substrates play a pivotal role in GHG emissions by inhibiting methanogens' activity and altering nitrogen transformation pathways. Temperature affects GHG emissions by directly influencing the activity of methanogens, nitrifiers, and denitrifiers. Furthermore, influent characteristics, such as organic carbon load, NH_4^+ , NO_2^- , NO_3^- , TN load, and C/N, can influence GHG emissions by promoting or inhibiting their production and oxidation. CWs are complex systems with various influencing factors, and comprehensively understanding the interactions of these factors is crucial for optimizing CW systems and minimizing their GHG footprint.

5. Conclusions and Prospects

Constructed wetland is an efficient and economical surface water treatment technology that uses the natural processes of plants, substrates, and microbes to treat wastewater. According to design structures and flow direction, CWs are divided into FWS CWs, HSSF CWs, VSSF CWs, and the combination of these, HCWs. However, CWs produce a lot of GHGs in the process of wastewater treatment, which significantly impacts global warming.

The impact of CWs on GHGs is complicated because they can produce a large amount of CO_2 , CH_4 , and N_2O as by-products or intermediate products in the process of animal and plant respiration, anaerobic fermentation of organic matter, oxidative stress response, nitrification and denitrification, DNRA, SND, denitrification by nitrifiers, denitrification by aerobic denitrifiers, etc., and transmit them into the atmosphere mostly through plants, forming sources of GHGs, resulting in the greenhouse effect. In contrast, they can also fix CO_2 from the atmosphere into sediments via plant photosynthesis, forming sinks of GHGs, and oxidize most of the CH_4 produced in CWs to CO_2 by aerobic and anaerobic oxidation, thus reducing CH_4 emissions.

CWs' overall performance depends on many factors, such as the type and age of CWs, plant, substrate, temperature, and influent characteristics. HCWs have higher nitrogen removal efficiency and fewer GHG emissions than single-type CWs. In the short term, CWs act as a source of GHGs, and with the growth of wetland age, GHG emissions are increasing, while over longer timescales (>100 years), CWs act as a sink of GHGs. Plant

presence and abundance have controversial consequences for GHG emissions, which may depend on plant specificity; *Cyperus papyrus* and *Cyperus alternifolius* provide aerenchyma to transport O₂ to the plant rhizosphere, promoting the oxidation of CH₄ in the micro-oxygen environment. *Iris pseudacorus* has a strong carbon sequestration ability and could cover the emission of nitrous oxide and methane, acting as the carbon sink. Plant roots secrete small molecular organic matter in the growing season, promoting GHG emissions, and many GHGs are released when plants are harvested. Adsorption substrate types, such as Fe-C, can increase methane and oxygen adsorption via activated carbon and compete with methanogens for substrate in the presence of iron-reducing bacteria, ultimately reducing CH₄ emissions. Temperature affects GHG emissions in CWs by influencing microbial activity and the succession of dominant bacteria. Low temperatures will reduce the CH₄ and N₂O emissions. High NH₄⁺, NO₂[−], and NO₃[−] loads can inhibit the aerobic oxidation of CH₄ and increase CH₄ emissions, but high NO₃[−] loads can also promote the anaerobic oxidation of CH₄, thereby reducing methane emissions and increasing CO₂ emissions. When the influent C/N is 5, the nitrogen removal efficiency is the highest, and the GHG emissions are the least.

The above factors affect the production, transport, and oxidation process of GHGs via various physical, chemical, and biological processes. Many studies have conflicting results on a single influencing factor because the single-factor relationship in the complex natural environment is insufficient to explain the differences in GHG emissions. However, most current studies focus on the influence of a single influencing factor on a single GHG. The source-sink effects and mechanisms of various comprehensive factors on GHGs in CWs are still unclear, and further research is needed. In addition, carbon fixation and GHG emissions of CWs jointly determine the impact of this technology on global warming. However, the current research seems to focus only on studying GHG emissions. It needs more measurement and research on the carbon balance of the whole system and the comprehensive greenhouse effect. According to the analysis, carbon sequestration by plant photosynthesis is the main way of carbon sequestration in CWs, which has both direct and indirect effects on the biogeochemical cycle of carbon, and these processes are closely related. There needs to be more research methods to ensure the differentiation and quantification of these processes, especially the microbial community-plant interactions involved in carbon sequestration and GHG emissions.

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