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Methane Release Driven by Algae Vital Activity

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Abstract: As a potent greenhouse gas, accurate estimation and regulation of methane's global emission budget is the key to addressing climate change. Conventional wisdom suggests that methane production is mainly confined to anaerobic environments, but recent studies have confirmed that algae can drive methane release through a variety of pathways. Although the current research clarifies the important role of algae in the methane cycle, it still faces challenges such as difficulty in quantifying the ecological contribution rate of each release pathway and unclear key molecular mechanisms. In-depth exploration of the laws and mechanisms of algae-driven methane release can not only improve the theoretical framework of the global methane cycle, but also provide scientific basis and new perspectives for ecosystem greenhouse gas emission control and carbon cycle regulation.

Keywords: methane; algae; nutrients; environment.

1 INTRODUCTION

Methane (CH_4) is the second largest greenhouse gas after carbon dioxide (CO2), but the assessment report of the United Nations Intergovernmental Panel on Climate Change (IPCC) states that CH4 per unit mass has a global warming potential. GWP) is 84 times that of CO2 on a 20-year scale and 28 times that of CO2 on a 100-year scale [1-3]. Methane exists in the atmosphere for a very short lifetime, only about 10-12 years, but atmospheric methane concentrations can respond relatively quickly to methane emission reduction activities, so it is extremely important to study methane release and its influencing factors [4].

At present, research on methane release in nature is mainly focused on wetland environments such as swamps and lakes and constructed wetlands such as rice fields [5-7]. Studies have shown that methane produced in underwater sediments is oxidized to CO2 by methanoxidizing bacteria living in the water layer, which largely inhibits the escape of methane from the water. Therefore, in general, the net accumulation of methane in water is the result of the combined action of these two types of microorganisms [8]. According to the different substrates used by methanogens, the methanogenic pathway is divided into three pathways: H2/CO2 (CO2 reduction) pathway, acetic acid fermentation pathway, and methyl compound cracking pathway [9]. Some studies have also shown that factors such as water temperature, pH, dissolved oxygen concentration, and nutrients may affect CH4 release flux to a certain extent [10-12].

Aquatic vegetation has been recognized as an important factor affecting CH4 emissions, as it can not only provide active organic carbon for the growth of methanogens, but also affect the activity of methanogens and the oxidation of CH4 by regulating the oxygen content of water and sediments [13-16]. As an important part of aquatic vegetation, algae have a relatively simple composition, a wide range of existence, high nutritional value and fast decomposition rate. Half of the substances in the algae are proteins, one-third are carbohydrates, and the rest are fats, vitamins, and trace elements [17]. The rapid decomposition rate allows algae to release large amounts of nitrogen and phosphorus nutrients into the water body in a short period of time, and the intensity of nutrient release increases with the increase of algae accumulation [18, 19]. In recent years, due to human activities and agricultural inputs of nutrients, water bodies have become eutrophic, which in turn leads to the massive growth, decline, decay and degradation of algae. The decomposition of algal detritus decay depletes dissolved oxygen in water on the one hand, and also releases large amounts of nutrients into the water on the other hand [20-22]. During the anaerobic decomposition of algae, complex organic matter such as proteins, fats, and carbohydrates in algal cells are further converted into amino acids, peptides, monosaccharides, etc. after hydrolysis and anaerobic fermentation, and then further decomposed by microorganisms to produce substances with smaller molecular weights [23], thereby providing substrates for methanogens. Therefore, algae growth and decay cause the degradation of large amounts of organic matter [24] and the release of methane [25, 26].

Algae play a non-negligible role in the release of methane. As primary producers in aquatic ecosystems, the growth, decay and degradation of algae can significantly change the physicochemical properties of water bodies, especially through their photosynthesis and respiration. At the same time, algae-derived organic matter produced by the decomposition of algae

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after death also provides an important carbon source for methane production [27-32]. These new findings suggest that algae may regulate methane release by affecting the water environment

2 Effects Of Algae-Driven Environmental Factors On Methane Release

As a key component of aquatic ecosystems, the growth and metabolic activities of algae have a profound impact on the surrounding environment [30-33]. The growth and metabolism rate of algae are inseparable from ambient temperature, and temperature also plays an important role in the methanogenesis process of methanogenesis. Under high light conditions, algae grow rapidly, increasing dissolved oxygen in the water and potentially inhibiting the formation of an anaerobic environment, thereby slowing down methane production and release. Algae can release oxygen through photosynthesis and consume carbon dioxide in water, changing the dissolved oxygen content and pH of the water body, which in turn affects the activity of methanogens [34, 35]. The decay and decomposition of algae becomes an important source of organic matter, providing sufficient substrate for methanogens to produce methanogens [36, 37]. Therefore, algae play a complex and important role in regulating methane release in water bodies through their life cycle activities and ecological effects.

Algae-driven methane release is a complex process influenced by various environmental factors. The following describes the role of algae in the formation and release of methane from three aspects: dissolved oxygen (DO), temperature and pH.

2.1 Dissolved Oxygen

Dissolved oxygen levels are not only important indicators for evaluating water self-purification capacity and biological activity status [38], but also a key factor in regulating methane release, and studies have shown that methane release flux is negatively correlated with dissolved oxygen concentration [39]. Several cofactors and enzymes involved in the metabolism of methanogens (such as CO dehydrogenase and acetyl-CoA synthase) are sensitive to oxygen when DO concentrations are higher than 10 mg·L-1, the activity of methanogens will be completely inhibited [40], so methane is the end product of the decomposition of organic matter under anaerobic conditions, which can only be produced in a strict anaerobic environment, so the concentration of dissolved oxygen in the environment will directly determine the yield of methane in the ecosystem [41, 42]. At the same time, the rate of methane oxidation is also closely related to the concentration of dissolved oxygen in the environment, and the increase of oxygen concentration is conducive to the aerobic oxidation of methane [43], and low dissolved oxygen concentration can increase the activity of methanogens, inhibit methane oxidation, and increase methane emissions [44].

Grossart et al. [45] demonstrated that methanogens can directly attach to algal cells, and algae may provide them with an anaerobic environment, thereby promoting typical CH4 production by methanogens. It has been found that about 85% of the dissolved oxygen (DO) in the water body is provided by algae through photosynthesis during the day, but at night, the oxygen consumed by algae needs to be respired, and the oxygen consumption even exceeds the amount of oxygen produced by algae photosynthesis during the day, which makes the sediment-water interface anaerobic [35], thereby promoting methane production. The decomposition of algae will increase the content of soluble organic carbon (DOC) in water and sediments, thereby promoting microbial respiration, leading to a decrease in dissolved oxygen content in the water, hypoxic or even anaerobic conditions [46, 47], increasing the activity of anaerobic microorganisms, especially methanogens, and preventing the reoxygenation process in the water body [48]. For example, macrofilamentous algae can increase DO concentrations in aquatic ecosystems through photosynthesis, while nocturnal respiration, decomposition of algal residues, and resulting microbial respiration will also significantly reduce DO content in surface sediments in the system [34]. Studies have shown that the DO content at the sediment-water interface differs significantly between day and night in the summer due to the diurnal photosynthesis-respiration process of macrofilamentous algae with high primary productivity [35].

Algae can release oxygen through photosynthesis to maintain the concentration of dissolved oxygen in water, which inhibits methane production to a certain extent. However, when algae cells stop photosynthesis at night or when there is not enough light, they turn to respiration to consume oxygen, causing the water to quickly change into a hypoxic or anaerobic state, which is more pronounced when algae overgrow. This change in environment provides favorable growth conditions for methanogens and promotes the release of large amounts of methane.

2.2 Temperature

It has been shown that CH4 production in methanogenic archaea (mainly in sediments)tends to be temperature-related when sufficient substrates are available [49, 50]. However, the mechanism of temperature on CH4 emissions is not clear. It is generally believed that the direct effect of temperature on methane release flux is achieved by changing the dissolved oxygen content of the water body, the activity and solubility of methanogens.

Temperature changes the content of dissolved oxygen in the water, and within a certain range, the dissolved oxygen content in the water decreases with the increase of temperature [51], and the increase in temperature increases the photosynthesis intensity of aquatic plants and phytoplankton in the water body, thereby consuming the CO2 content of the water body, releasing O2, and changing the dissolved oxygen content of the water body [52]. Therefore, temperature can affect methane flux by changing the dissolved oxygen content of the water. In general, methanogens can only maintain relatively high viability at 0-35°C, and their activity will be inhibited when the ambient

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temperature is lower or higher than the optimal temperature for methanogenic functions [53]. In addition, changes in temperature will also affect the emission pathways of CH4 in aquatic ecosystems. When the water temperature is high, the accumulation of CH4 in the sediment is greater than its diffusion, so it is easy to cause CH4 in the sediment to be oversaturated and form bubbles to be released into the water body [54]. Not all CH4 enters the atmosphere because part of CH4 is oxidized by microorganisms, a process that is also related to temperature [49, 55, 56].

Temperature also indirectly affects methane flux through the effects on aquatic plants in aquatic ecosystems, such as algae, which generally increases the growth rate and photosynthesis efficiency of algae as water temperature increases, thereby promoting the production of dissolved oxygen in water bodies [35]. However, under anaerobic or hypoxic conditions, the activity of methanogens increases significantly with increasing temperature, as higher temperatures can accelerate their enzymatic reactions and increase the rate of methane production [41]. Therefore, although algal activity can inhibit some methane production by increasing dissolved oxygen, the mass death and deposition of algae may actually exacerbate methane release when water stratification or dead zones are formed due to high temperatures and eutrophication [46, 47]. The presence of large filamentous algae can also affect the temperature of the water environment. Most of the solar energy absorbed by the algae will be converted into thermal energy, which will be consumed during water transpiration or re-enter the water by increasing the temperature of the algal cushion cluster. Therefore, during the period of vigorous algal growth, the water temperature in the macrofilamentous algae habitat will be slightly higher than that in the clear water area, which also affects the community structure diversity, metabolic rate, and substrate supply of methanogens in aquatic ecosystems [57].

Temperature affects methane flux by affecting the concentration of dissolved oxygen in water, the activity of microorganisms such as methanogens, and the solubility of methane. Algae also play a role in this.

2.3 PH

pH is an important parameter to measure the pH of water, and it has a significant impact on algae growth and methane release [33, 58]. It is important to understand the changes produced by CH4 through the response of CH4 production potential to pH changes. The activity of methanogens is usually best in neutral or slightly alkaline environmental conditions and is very sensitive to changes in pH [59].

Methanogens are sensitive to pH in the environment, with an optimal pH range of around 6.0 – 8.0, but diversity also exists at extreme pH [60]. The metabolic pathways of methane production at different pH environments are also different [61]. Studies have found that when the pH drops to 3.8, the methane production pathway changes from acetic acid fermentation methanogenesis to hydrotrophic methanogenesis [53]. It has also been found that the methane production pathway is hydrotrophic when pH is 3.9 – 4.6, and CH4 produced by acetic acid fermentation can account for 60%~68% of the total production when pH is 6.0 – 4.8, and methanogens through hydrotrophic and acetic acid methanogenic pathways exist simultaneously at pH 5.0 – 5.3 [62]. On the one hand, methanogens are more sensitive to changes in pH in the environment, while on the other hand, they can survive in extreme pH environments, and the methane production pathways in the environment are different when the pH is different.

Most algae have some adaptive range to pH and usually grow in neutral or slightly alkaline conditions [58]. Photosynthesis by algae consumes carbon dioxide in water, leading to an increase in pH that affects methane production and release [58]. Algae decay and decomposition produce acidic substances, leading to a drop in water pH [63]. This change may affect the activities and metabolic processes of other organisms in the water body, indirectly affecting methane production. Methanogenic bacteria are usually most desirable in neutral or slightly alkaline environmental conditions and are very sensitive to changes in pH [33]. For example, in acidic environments, the activity of methanogens may be inhibited, while the activity of methanogens may be enhanced, reducing the net release of methane. Under certain acidic conditions, the methanogens in the culture will be irreversibly inactivated [64].

An appropriate pH not only promotes photosynthesis and growth of algae, but also maintains the balance of microbial communities in the water, including the ratio of methanogens and methanogens. However, when water is polluted or environmental factors change and the pH deviates from the appropriate range, the growth of algae may be inhibited, and the structure and function of the microbial community may also be changed, which in turn affects methane production and conversion.

In summary, algae-driven environmental factors, including temperature, dissolved oxygen, and pH, have complex and far-reaching effects on methane release. Algae regulate the dissolved oxygen level and pH of water through photosynthesis and respiration, which in turn affects the activity of methanogens and methanogens, as well as the formation and conversion of methane. In actual water environment management, the interaction between these factors should be fully considered, and comprehensive measures should be taken to regulate the growth and metabolic activities of algae to reduce the emission of greenhouse gases such as methane and protect the health and stability of the water environment.

3 EFFECTS OF NUTRIENT CHANGES ON METHANE RELEASE IN ALGAE-DRIVEN AQUATIC ECOSYSTEMS

Algae belong to lower plants, and the decay and decomposition process of algae is very complex, including hydrolysis of algal tissue, dissolution of mineral components and soluble organic matter, enzymatic hydrolysis and biodegradation of various organic components, etc. The basic process can be divided into two stages, the first stage is the rapid disintegration of algal residues and the release of organic matter, and the second stage is the slow decomposition of poorly soluble organic matter under the action of microorganisms and extracellular enzymes [65]. Bloom algae will gradually accumulate and accumulate in large quantities under suitable meteorological conditions (such as temperature, light, wind, etc.), resulting in a decrease in dissolved oxygen concentration. In general, the concentration of organic matter released into water during algae accumulation and decomposition shows a continuous upward trend [66, 67].

Algal decay and decomposition drive the release of CH4, and algal succession processes intensify CH4 production. After the bloom caused by eutrophication of water bodies, the decline of a large number of algae became an important factor affecting the production of CH4 [68-70]. On the one hand, algae play an important role in maintaining the stability of water ecosystems, and the normal growth stage of algae can fix a large amount of CO2 as a carbon sink in water bodies through primary production. On the other hand, a series of biochemical processes such as algal decay and algal organic matter (AOM) mineralization also provide sufficient substrates for methanogens. In eutrophicated water bodies with high primary productivity, CH4release is significantly increased [71, 72].

During algal blooms, the released AOM will have a significant impact on the environment of aquatic ecosystems. It is worth mentioning that the content and composition of algal-derived organic matter produced by the decomposition of different algae contribute differently toCH4 emissions [47, 73]. Meersche et al. [74] labeled inorganic carbon with 13C and found that algae can contribute up to 60% of carbon to water during bloom formation, which can be used as substrates for methane production. Shang Lixia et al. [19] found that cyanobacterial decomposition releases a large amount of organic matter and N and P nutrients during the decomposition of high-density cyanobacteria, which worsens water quality, and this effect intensifies with the increase of algae density. It also provides nutrients for methanogens. Shi et al. [75] also found that the particulate carbon, nitrogen, and phosphorus were gradually decomposed into dissolved states during the aerobic decay of cyanobacteria, and the coupling relationship between carbon, nitrogen, and phosphorus was constantly changing. Provides a substrate for methane production. Macrofilamentous algae can fix nitrogen in wetlands as nutrients needed for their growth and release excess nitrogen into water bodies during the decay and decomposition period, thereby affecting the nitrogen cycle process in ecosystems [76-78]. However, this process also affects the production and release of CH4 in water [79]. Studies have shown that increased nitrogen in water due to algae nitrogen release will promote CH4 formation. On the one hand, the increase in ammonia nitrogen content in water due to the increase in nitrogen can reduce the oxidation of CH4 by methane-oxidizing bacteria [80], thereby increasing the potential release flux of CH4. However, nitrates in water can increase osmotic pressure and inhibit the activity of methane-oxidizing bacteria, thereby reducing their consumption of CH4 in water [81]. In addition, nitrite toxicity caused by nitrification or denitrification processes also inhibits the oxidation process of CH4 [82]. On the other hand, the input of higher nitrogen-rich clastic species slowed down the carbon restriction of microorganisms, thereby enhancing methanogenic activity and ultimately increasingCH4 production.

Dissolved organic carbon (DOC) is considered one of the most important factors affecting CH4 production under anaerobic conditions [83]. On the one hand, DOC in sediments can be directly converted into acetate and CO2/H2 substrates required for the formation of CH4 through a series of biochemical processes, and on the other hand, the process of DOC decomposition to DIC requires partial oxygen consumption, thus creating a good anaerobic environment for methanogens [34]. Tranvik et al. [84] found that higher DOC concentrations in water bodies can increase CH4 production and emissions, Keller et al. [85, 86]DOC was found to promote the activity of methanogens in sediments, thereby increasing CH4 production in aquatic ecosystems. Studies have shown that under nutrient-sufficient environmental conditions, algae can release 19% of the total carbon fixed by photosynthesis into the water body, and the primary productivity of algae is positively correlated with DOC content [87]. Some studies have also shown that when algae decay and decompose in the later stages of growth, their degradation products include acetate and other fermentation products, which also stimulate the activity of methanogens and the production of CH4 [88]. West et al. compared the effects of algae and terrestrial plants on methane production and found that the methane production rate increased rapidly after the addition of algae, while the methane production rate increased slowly but for a long time after the addition of terrestrial plants [89].

Algae decay and decomposition will produce algae-derived organic matter. Algae-derived organic matter produced by algae has a significant impact on methane release by providing methanogenic substrates, changing the physical and chemical properties of water bodies, affecting the number and activity of methanogens, and promoting methane release.

4 EFFECTS OF ALGAE-DRIVEN ELECTRON ACCEPTORS ON METHANE RELEASE

The growth, decay, and degradation processes of algae indirectly affect the release of methane by changing the electron acceptor conditions in the water. During the growth phase, the abundance of electron acceptors inhibits methane production; In the decay and degradation stages, methane production and release begin to increase with the gradual depletion of electron acceptors and the formation of an anaerobic environment.

The substances produced by algae decomposition can oxidize methane by acting with different electron acceptors (oxygen, NH4+, nitrate/nitrite, sulfate, Fe(III) and Mn(V), etc.). It affects methane conversion to varying degrees [30, 31, 90]. Recent studies have found that microorganisms such as nitrate-reducing bacteria and sulfate-reducing bacteria in sediments can use different carbon sources such as monomeric cells, fatty acid alcohols, and acetate to reduce different electron acceptors (TEAs), such as nitrates, sulfate ions, and trivalent iron ions, into ammonium ions, acidic volatile sulfur (AVS), and ferrous ions, to obtain electrons to complete their respiration, whichcauses great competition for the substrates required for CH 4 production. and ultimately inhibit the production of CH4 [91, 92].

5 CONCLUSION

There is a potential impact of algae on the production of CH4 gas. The growth, decay and degradation processes of algae affect the dissolved oxygen, organic matter, nutrients, pH, temperature, and microbial population of the water body, and these factors are important factors for the production of CH4. Methane anaerobic oxidizers use methane as a substrate to oxidize methane by acting with different electron acceptors (oxygen, NH4+, nitrate/nitrite, sulfate, Fe(III) and Mn(V)), which affects methane conversion to varying degrees. The impact of algae as primary producers on the biogeochemical cycle of CH4 has spatiotemporal dynamics, and the production and control factors of CH4 driven by algal bloomsshould be the focus of attention.

However, it is worth noting that important results have been made in the influence and mechanism of microalgae on methanogenesis in freshwater aquaculture ponds in southern tropical and subtropical monsoon climates in China, but there are few studies on methane production and release in northern aquaculture ponds. Therefore, under the trend of continuous warming and northward movement caused by climate change, it is particularly necessary to provide more data to provide scientific assessment of the contribution of macroalgae as sinks and sources of carbon cycle in different ecological types, given the clear temperature changes in the north, the intensification of eutrophication in mariculture ponds, and the proliferation of macroalgal blooms.

More importantly, in the process of continuous exploration, people have found that anaerobic is not the only condition for methane production in nature, and methane production can also be carried out under aerobic conditions. Microorganisms change their metabolic pathways to aerobic metabolism by changing their related genes, and the researchers also photographed methanogenic archaea attaching to algae in the upper water of the lake through fluorescence in situ hybridization (FISH) technology, and algal photosynthesis can provide methanogens with an "umbrella" for their growth of "anaerobic microecological niches" suitable for their growth, and transfer methanogenic substrates directly to methanogens to produce methane. There are too many unrecognized scientific questions about the effects and mechanisms of macroalgal blooms on methane emissions that deserve to be studied.

In summary, given the important role of algae as primary producers in the carbon cycle, it is necessary to enrich more research on the impact of algae on methane release.

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