Proceedings of the 3rd International Conference on Modern Medicine and Global Health
DOI: 10.54254/2753-8818/68/2025.20031

Current Status of Research on Marine Nitrous Oxide Greenhouse Gases

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Abstract: Nitrous oxide (N_2O) is a potent greenhouse gas with a global warming potential 200 times that of carbon dioxide (CO_2) [1]. N_2O not only enhances the greenhouse effect but also breaks down in the stratosphere to produce nitrogen oxides (NO), which catalyze the destruction of the ozone layer [2]. This article reviews studies on N_2O, exploring its distribution and generation mechanisms in various marine regions and discussing its environmental impact.The ocean is the largest natural source of N_2O, with significant contributions from oxygen-deficient zones (ODZs) where high rates of nitrification and incomplete denitrification occur. Other high-oxygen areas, which cover 97% of the ocean, have different production mechanisms that are not well understood [4].This article aims to summarize the formation mechanisms, distribution, and effects of N_2O, providing an overview of its current research status as a greenhouse gas.

Keywords: nitrous oxide, greenhouse gas, global warming potential, Oxygen-deficient zones (ODZs), ocean, Environmental impact.

1. Introducion

Nitrous oxide (N_2O) is a significant greenhouse gas with a global warming potential approximately 200 times greater than that of carbon dioxide. Its dual environmental impact includes contributing to the greenhouse effect and depleting the ozone layer through the production of nitrogen oxides in the stratosphere. The ocean is one of the largest natural sources of N_2O, with key production processes occurring in oxygen-deficient zones (ODZs) and areas of nitrification and incomplete denitrification. This study reviews the distribution, generation mechanisms, and environmental consequences of N_2O in marine ecosystems, emphasizing the importance of understanding its role in global warming and ozone depletion.

2. The source and generation mechanism of nitrous oxide

Nitrous oxide (N_2O) is generated in the ocean through various biogeochemical processes. These processes mainly include nitrification, denitrification, anaerobic ammonia oxidation, etc. Each mechanism has its unique biochemical pathway and environmental dependence.

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DOI: 10.54254/2753-8818/68/2025.20031

2.1. Nitrification

Nitrification is one of the main pathways for the generation of N_2O in the ocean. This process involves two steps:

2.1.1. Ammonia oxidation

Ammonia is oxidized to nitrite (NO_2^-), catalyzed by ammonia-oxidizing bacteria (AOB) and ammonia-oxidizing archaea (AOA). The reaction formula is as follows:

$NH_3 + O_2 \rightarrow NO^- + 3H^+ + 2e^-$

2.1.2. Nitrite oxidation

Nitrite is further oxidized to nitrate, which is catalyzed by nitrite-oxidizing bacteria (NOB). The reaction formula is as follows:

$NO_2^- + O_2 \rightarrow NO_3^-$

During the process of ammonia oxidation, N_2O is generated as a byproduct. Ammonia-oxidizing bacteria can produce N2O through the following two pathways during the ammonia oxidation process:

- Hydrogen oxidase pathway: Under the catalysis of hydrogen oxidase (HAO), ammonium hydroxide (NH_2OH) is partially oxidized to produce N_2O.
- Nitrate reduction pathway: Under low oxygen conditions, some nitrite is reduced to produce N_2O.

The literature indicates that nitrification contributes significantly to N_2O generation, especially in subtropical and tropical upwelling regions and coastal eutrophication zones [5].

2.2. Denitrification

Denitrification is the process in which nitrate is reduced to nitrogen by denitrifying bacteria in an anaerobic environment. This process is also divided into several steps:

- Nitrate reduction: Nitrate (NO_3^-) is reduced to nitrite (NO_2^-).
- Nitrite reduction: Nitrite is further reduced to NO and nitrous oxide (N_2O).
- Nitric oxide reduction: NO is further reduced to N_2O.
- Nitrous oxide reduction: N_2O is ultimately reduced to nitrogen (N_2).

Each step in denitrification may produce N_2O, and the proportion of N_2O generated as an intermediate is greatly influenced by environmental conditions such as oxygen concentration, carbon source, and pH value. [6].

2.3. Anaerobic ammonia oxidation

Anammox directly converts ammonia and nitrite into nitrogen in anaerobic environments. The reaction formula is as follows:

$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$

Although anaerobic ammonia oxidation mainly generates nitrogen (N_2), a small amount of N_2O may also be produced during this process. The specific mechanism may be related to the incomplete reduction of intermediate NO. The literature suggests that anaerobic ammonia oxidation's contribution cannot be ignored in specific regions such as oxygen minimum zones (ODZs) [7].

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2.4. Other generation pathways

In addition to the main pathways mentioned above, the generation of N_2O may also be achieved through other pathways, such as:

- Heterotrophic nitrification-denitrification: Some heterotrophic bacteria are capable of simultaneously nitrifying and denitrifying during organic matter degradation, thereby producing N_2O.
- Photochemical processes: Some studies have shown that dissolved organic matter in the ocean surface may generate N_2O through photochemical reactions under strong light irradiation.

3. Sources of nitrous oxide in different regions

Characterization of different regions

3.1. Arctic region

Toyoda et al. (2021) pointed out in their study that gas exchange in the Arctic Ocean is highly sensitive to global warming, particularly as the reduction in sea ice cover enhances gas exchange between the ocean and the atmosphere. In the Arctic, N_2O is mainly produced through two microbial processes: nitrification under aerobic conditions and denitrification under anaerobic conditions. During nitrification, ammonia-oxidizing bacteria (AOB) and ammonia-oxidizing archaea (AOA) generate N_2O through ammonia oxidation, while during denitrification, denitrifying bacteria produce N_2O during nitrate reduction to nitrogen (N_2).

3.2. Eastern Tropical South Pacific

Casciotti et al. (2018) studied the N_2O cycle in the eastern tropical South Pacific and found that the N2O concentration and nitrogen isotope composition in the region are influenced by oxygen content and water structure. Research has shown that in low-oxygen regions, the production of N_2O is mainly driven by nitrification and denitrification processes. In these regions, denitrification dominates at lower oxygen concentrations, while nitrification is more pronounced at higher oxygen concentrations.

3.3. Eastern Tropical North Pacific

Kelly et al. (2021) investigated the N_2O cycling mechanism in the eastern tropical North Pacific, emphasizing the influence of the minimum oxygen layer (ODZ) on the distribution of N_2O. In ODZ, due to severe oxygen deficiency, denitrification and anaerobic ammonia oxidation (anammox) are the main pathways for N_2O production.

N_2O production also varies across different regions due to differences in microbial processes and environmental conditions. In the Arctic Ocean, N_2O is primarily produced by nitrification and denitrification, with gas exchange enhanced by sea ice reduction. The eastern tropical South Pacific sees N_2O production influenced by oxygen levels, with denitrification dominating in low-oxygen areas. In the eastern tropical North Pacific, the oxygen minimum zone (ODZ) facilitates N_2O production through denitrification and anammox.

3.4. Mechanism of N_2O generation and consumption in the Southern Ocean

Researchers collected water samples from three locations in the Southern Ocean (at 61° S, 64° S, and 66.15° S) and measured the N_2O isotope ratios. This included examining how these ratios vary with depth and calculating the site preference (SP).

Nitrification process

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The nitrification process mainly occurs in shallow water bodies, and the generated N_2O has a characteristic isotopic ratio. Ammonia oxidation and nitrate oxidation are two key steps, completed by ammonia oxidizing bacteria and nitrate oxidizing bacteria, respectively.

Denitrification process

The denitrification process plays an important role in the middle layer of water, especially in areas with low oxygen content. The denitrification process not only consumes N_2O but also generates N_2O through nitrate reduction, which has a high SP value and is a hallmark of the denitrification process.

The results indicate that the generation and consumption of N_2O are controlled by various biogeochemical processes, and the relative importance of these processes varies in different depths of water. The nitrification process in shallow water and the denitrification process in middle water jointly affect the distribution and isotopic characteristics of N_2O.

4. Planar and vertical distribution of nitrous oxide in the ocean

The distribution of nitrous oxide (N_2O) in the ocean varies both horizontally and vertically. These differences are influenced by various physical, chemical, and biological factors, such as water temperature, oxygen content, nutrient concentration, and microbial activity.

i. Planar distribution

1. Global distribution of marine N_2O

Tropical and subtropical upwelling areas: These areas become eutrophic due to the increase in nutrients, promoting the production of phytoplankton and the degradation of organic matter, thereby enhancing the activity of nitrification and denitrification. Typical regions include the Arabian Sea and the coastal upwelling zone of Peru, where N_2O concentrations are high [11].

Polar regions: Polar regions typically have lower N_2O concentrations, but local areas may experience higher N_2O concentrations due to seasonal ice sheet melting and nutrient inputs [12].

Mid-ocean: The concentration of N_2O in the mid-ocean is generally lower because these regions typically have less nutrients and relatively low biological activity.

2. Coastal areas

Coastal areas typically have high concentrations of N_2O, mainly due to eutrophication caused by human activities such as agricultural runoff and sewage discharge, which increase nitrogen input and promote nitrification and denitrification [14].

Typical high N_2O concentration areas include estuaries, lagoons, and continental shelves.

ii. Vertical distribution

The research team collected water samples at three stations in the Southern Ocean (61°S, 64 ° 66°S, and 66.15°S) and determined the N_2O isotope ratio using gas chromatography-isotope ratio mass spectrometry (GC-IRMS).

1. Surface water body (aerobic zone 0-350 meters)

In shallow water bodies, the concentration and isotopic ratio (especially SP values) of N_2O indicate that nitrification processes (i.e. ammonia oxidation and nitrate oxidation) are the main production mechanisms of N_2O.

- Surface water bodies usually have sufficient dissolved oxygen, and the generation of N_2O is mainly through nitrification. In areas with strong photosynthesis, an increase in oxygen may inhibit denitrification, thereby reducing the generation of N_2O [6].
- The surface N_2O concentration is generally low, but in eutrophic coastal areas and upwelling areas, N_2O concentration may be higher.

2. Middle water body (minimum oxygen zone, ODZs 350-1000 meters)

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The oxygen minimum zones (ODZ) are key regions for the generation of N_2O. In these areas, extremely low oxygen concentrations facilitate anaerobic processes such as denitrification and anaerobic ammonia oxidation, which produce substantial amounts of N_2O .

Typical ODZ regions include the Arabian Sea, Southeast Pacific, and the coastal waters of California, where N_2O concentrations are significantly higher than in other sea areas.

The observed changes in N_2O concentration and isotopic ratio in the middle water column demonstrate the dynamic balance of N_2O production and consumption. At this depth, the isotopic characteristics of N_2O indicate the influence of partial denitrification processes, specifically the reduction of nitrate to nitrous oxide and nitrogen (N_2).

3. Deepwater bodies (350-1000 meters)

Deep water bodies usually have sufficient oxygen and lower concentrations of N_2O, with a relatively stable isotopic ratio. This indicates that N_2O in deep water is mainly controlled by water mixing processes, while biogeochemical processes have a relatively small impact. Nitrification is the primary pathway for N_2O generation, but due to the slow degradation rate of organic matter, the amount of N_2O produced is limited.

However, in certain special areas, such as near deep-sea hydrothermal vents, there may be a local increase in N_2O concentration due to unique geochemical processes occurring in these environments.

iii. Characteristics of N_2O content in the oxygen thermocline, aerobic zone, and coastal zone

1. Oxygen thermocline

The oxygen thermocline refers to a water layer with a rapid change in oxygen concentration. In this layer, the sharp transition from high to low oxygen levels makes the production and consumption processes of N_2O relatively active, often resulting in a significant peak in N_2O concentration [15].

In the upper part of the oxygen thermocline, nitrification dominates, while in the lower part, denitrification strengthens, leading to an increase in N_2O generation.

2. Aerobic zone

- Aerobic zone refers to the area of seawater with sufficient dissolved oxygen. In these regions, N_2O generation is mainly carried out through nitrification. Under high oxygen conditions, denitrification is inhibited and N_2O generation is relatively less.
- Typical aerobic regions such as the surface waters of the Atlantic and Pacific oceans have low and stable N_2O concentrations.

3. Coastal areas

- The concentration of N_2O in coastal areas is significantly influenced by terrestrial inputs, which is highly shown in horizontally. Agricultural runoff and urban sewage discharge increase nitrogen input, promote nitrification and denitrification processes, and thus increase the generation of N_2O.In estuaries and lagoon areas, due to high nutrient concentrations and strong biological activity, N_2O concentrations are usually high. [14].

For example, the Bay of Bengal, influenced by monsoonal inputs and high biological productivity, also shows elevated N_2O concentrations, highlighting the impact of regional factors on N_2O distribution.

5. The impact of nitrous oxide on the ocean environment

1. Greenhouse effect

N_2O is one of the important greenhouse gases, with a significantly higher global warming potential than CO_2. The increase in N_2O concentration will lead to more absorption of longwave radiation in the atmosphere, thereby enhancing the greenhouse effect and causing global climate warming. Toyoda et al. (2021) pointed out that the global warming potential of N_2O is 200 times that of CO_2.

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Therefore, although the concentration of N_2O in the atmosphere is much lower than that of CO_2, its contribution to global warming cannot be ignored.

2. Ozone layer depletion

N_2O decomposes into NO in the stratosphere, which catalyzes the decomposition of ozone molecules, thus damaging the ozone layer. The destruction of the ozone layer also has complex feedback effects on the climate system, such as altering the temperature structure of the stratosphere and troposphere, affecting atmospheric circulation and climate patterns.

3. Ocean acidification

The increase of N_2O can also indirectly affect ocean acidification. Although N_2O itself does not directly cause acidification, the intensification of greenhouse effects can alter the carbon cycle of the ocean, increase the content of CO_2 in the ocean, and accelerate ocean acidification. The impact of ocean acidification on marine organisms and ecosystems is significant.

For instance, pteropods, a type of planktonic snail, are highly sensitive to ocean acidification. Laboratory experiments have shown that increased CO_2 levels cause their shells to dissolve.

4. Water pollution

Nitrogen pollutants in water bodies may also generate N_2O through denitrification, further increasing the concentration of N_2O in the atmosphere.

One example of the impact of nitrous oxide (N_2O) on aquatic ecosystems is that elevated N_2O levels can contribute to hypoxia, which reduces the oxygen available for fish and other aquatic organisms, leading to increased mortality and impaired reproductive success. [18].

5. Human health

The direct impact of N_2O on human health is relatively small, but its indirect impact cannot be ignored. For example, the destruction of the ozone layer will lead to more ultraviolet radiation reaching the surface, thus increasing the incidence rate of skin cancer, cataracts, and other diseases.

6. Ecosystem

The emissions of N_2O have significant impacts on marine ecosystems. The increase of N_2O in marine ecosystems will affect the survival and ecological balance of marine organisms through ocean acidification and greenhouse effects. For example, the degradation of coral reefs and changes in the population of marine organisms can have profound impacts on the health and stability of marine ecosystems.

6. Outlook for future changes in nitrous oxide greenhouse gases

As an important source of N_2O, the generation and release of the ocean are influenced by various factors. Future climate change and human activities will further affect ocean N_2O emissions.

6.1. The dominant role of natural sources in N_2O emissions

In the future, marine natural sources will continue to be an important contributor to global N_2O emissions. The following factors will strengthen the dominant role of natural sources:

- Ocean change: Global warming will lead to an increase in ocean temperature, enhancing nitrification and denitrification processes, thereby increasing the generation of N_2O [5].
- Upwelling zone changes: Changes in the upwelling zone will affect the supply of nutrients and alter the generation and release patterns of N_2O. For example, tropical upwelling areas may become more intense due to climate change, thereby increasing N_2O emissions.

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6.2. Expansion of Oxygen Minimum Band (ODZ)

6.2.1. Formation and Expansion of ODZ

The Oxygen Minimum Zone (ODZ) refers to regions in the ocean where oxygen concentrations are extremely low, typically located at depths of 200-1000 meters. These hypoxic areas form due to the high consumption of oxygen from the degradation of organic matter and the oxidation of microorganisms.

In recent years, climate change has increased ocean warming and stratification, reducing the vertical transport of oxygen and leading to the expansion of ODZs.

6.2.2. Impact of ODZ Expansion on N_2O Generation

The expansion of ODZs significantly affects the generation and emission of N_2O:

- Enhanced Denitrification: In anaerobic environments, denitrification becomes more active, producing more N_2O. In ODZs, during the reduction of nitrate to nitrogen, N_2O accumulates as an intermediate product [11].
- Increased Anaerobic Ammonia Oxidation: The expansion of ODZs also provides favorable conditions for anaerobic ammonia oxidation, which, although contributing relatively less to N_2O generation, still plays a role[7].

6.2.3. Future Trends

With the intensification of climate change, ODZs are expected to expand further, particularly in regions like the Eastern Pacific and the Arabian Sea. This expansion will likely lead to a significant increase in N_2O generation and emissions, impacting the global N_2O budget.

7. Conclusion

Studying ocean nitrous oxide as a greenhouse gas is crucial as it has significant impacts on global warming and ozone depletion. In terms of global warming potential, nitrogen oxides have a power approximately 200 times that of carbon dioxide and play a crucial role in stratospheric ozone depletion, forming nitrogen oxides (NOx) during decomposition [1].

Nitrification and denitrification are the main biological processes that produce nitrous oxide (N_2O) in the ocean. Besides, anaerobic ammonia oxidation (anammox) also plays a role in ODZs. Additionally, heterotrophic nitrification-denitrification and photochemical processes may contribute to N_2O formation.

The distribution of nitrogen oxides in the ocean varies both horizontally and vertically. Horizontally, nitrogen oxide concentrations are high in subtropical and tropical upwelling regions due to enhanced biological productivity and organic degradation. In polar regions, levels are usually low but can increase seasonally due to ice melt. Coastal areas often show elevated nitrogen oxides due to eutrophication from anthropogenic nutrient inputs. Vertically, the distribution of nitrogen oxides varies with depth: In surface water (0-350 meters) areas, nitrification is dominant. Coastal and upwelling areas may have higher levels due to nutrient availability. In the mid water (ODZ) (350-1000 meters), low oxygen environments in the oxygen minimum zone (ODZ) promote denitrification and anaerobic ammonia oxidation, making this a significant source of nitrogen oxides. In the deep water (>1000 meters), nitrogen oxide levels are generally low due to decreased biological activity and slower organic degradation. However, local increases can occur near hydrothermal vents and other unique environments.

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The ocean, as a major natural source of nitrogen oxides, may expand its role with climate change. Upwelling and organic matter degradation will continue driving N_2O production.Climate change-induced hypoxia is expected to expand ODZs, increasing areas favorable for denitrification and anaerobic ammonia oxidation, thus raising N_2O emissions.

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