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Article

Mitigating nitrous oxide emissions through iron amendments in water-saving irrigated paddy fields: A review

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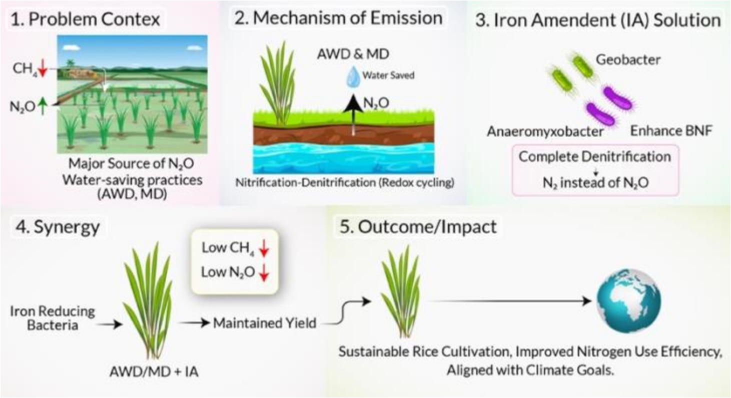

Highlights

- *Irrigation-saving techniques, e.g., AWD and MD, cut CH_4 but sharply increase N_2O emissions in paddy soils.*
- *Iron (Fe) amendments stimulate diazotrophs, lowering mineral N for N_2O.*
- *Fe-based amendments reduce nitrification and N_2O by ~40%.*
- *Fe^{2+} supplies electrons for complete $N_2O \rightarrow N_2$ reduction during denitrification.*
- *Integrating Fe amendments with AWD and MD balances N_2O, yield, and water use in rice ecosystem.*

Abstract

Rice cultivation is a major contributor to agricultural nitrous oxide (N_2O) emissions, a greenhouse gas with a global warming potential approximately 300 times greater than carbon dioxide (CO_2) and an atmospheric lifetime of ~121 years. Although water-saving irrigation practices, including Alternate Wetting and Drying (AWD) and Mid-Season Drainage (MD), effectively reduce methane (CH_4) emissions by up to 27.6% and decrease irrigation water use by 15–30%, they often intensify soil aeration and stimulate microbial nitrification-denitrification, leading to substantial increases in N_2O emissions. Reported increases range from 28.8% to more than 16-fold, with specific studies showing rises from 0.02 to 0.51 kg N_2O-N ha^{-1} under AWD and up to 242% under MD. These trade-offs threaten the long-term sustainability of water-saving rice systems. Iron-based soil amendments (IA) have emerged as a promising mitigation strategy to counteract these elevated N_2O emissions. For instance, iron (Fe) powder enhances the activity of Fe-reducing bacteria, such as *Geobacter* and *Anaeromyxobacter*, generating Fe^{2+} and lowering the soil's redox potential, which promotes the complete reduction of N_2O to N_2. Furthermore, other Fe amendments, including Fe-modified biochar and soluble ferrous iron (Fe^{2+}), help mitigate N_2O emissions by immobilizing NH_4^+, reducing the populations of ammonia-oxidizing bacteria, and supplying surplus electrons that enable

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denitrifiers to fully reduce N_2O to N_2. Empirical studies show that Fe-based amendments can reduce N_2O emissions by ~40% (iron-slag silicate fertilizer) and lower nitrification rates from 9.38 to 5.43 μg N g^{-1} d^{-1} when applied as Fe-modified biochar. Iron powder also enhances atmospheric N fixation, reducing reliance on synthetic nitrogen fertilizers. Integrating IA with AWD and/or MD, therefore, offers a synergistic pathway to sustain the benefits of water-saving irrigation while minimizing unintended increases in N_2O emissions. Field-scale, multi-season studies are still needed to validate long-term impacts and assess residual Fe behavior, but current evidence demonstrates strong potential for these combined strategies to support climate-resilient, low-emission rice production aligned with global mitigation goals.

1 Introduction

Nitrous oxide (N_2O) is one of the most potent and persistent greenhouse gases, with a global warming potential approximately 300 times greater than that of carbon dioxide (CO_2) over a 100-year timescale and an atmospheric lifetime of around 121 years (Reay, 2015; Griffis et al., 2017). Beyond its climate-warming effect, N_2O also contributes significantly to stratospheric ozone layer depletion, intensifying its environmental impact (Timilsina et al., 2020). Agriculture remains the dominant source of anthropogenic N_2O emissions, largely due to microbial transformations of nitrogen, primarily nitrification and denitrification, in intensively managed soils (Chataut et al., 2023). The primary mechanism of N_2O generation in paddy soils is the alternation between aerobic and anaerobic conditions, which supports both nitrification and denitrification. During aerobic phases, nitrifiers oxidize ammonium (NH_4^+) to nitrate (NO_3^-), releasing N_2O as a by-product. Conversely, under anaerobic conditions, denitrifiers reduce NO_3^- to dinitrogen gas (N_2) again producing N_2O as an intermediate (Xu et al., 2017; Ni et al., 2023). This redox fluctuation, characteristic of rice cultivation practices, stimulates both pathways, often enhancing N_2O emissions.

Among agricultural systems, rice cultivation is particularly critical due to its global scale, intensive water and nitrogen use, and complex soil biogeochemistry. As the second most widely grown cereal crop, rice sustains nearly half of the world's population and contributes over 20% of global calorie intake (Hashim et al., 2024). Asia accounts for more than 90% of global rice production, and in Bangladesh, rice occupies 75% of the total cropped area and 80% of irrigated land (Ministry of Food, 2023; BRKB, 2024). These extensive rice systems are major contributors to agricultural greenhouse gas (GHG) emissions, not only methane (CH_4) but also N_2O (Tariq et al., 2017; Xuan et al., 2025). While CH_4 emissions from flooded paddies have historically received greater attention, recent studies estimate that rice ecosystems contribute approximately 35.24% of global agricultural N_2O emissions, with irrigated rice systems responsible for 76.9% of that share (Song et al., 2023).

To address both CH_4 emissions and water scarcity in rice cultivation, water-saving irrigation practices such as Alternate Wetting and Drying (AWD) and Mid-season Drainage (MD) have been increasingly promoted. These techniques involve periodic drying of paddy fields, which shortens the duration of anaerobic conditions that favor CH_4 formation and thereby mitigates CH_4 emissions. AWD, in particular, can reduce CH_4 emissions by up to 27.6% and irrigation water use by 15–30%, while maintaining or improving yield and soil quality (Sriphirom and Rossopa, 2024; Phoeurn, 2024; Mote et al., 2021). Furthermore, Karki et al. (2022) reported that AWD reduced the yield-scaled global warming potential (GWP) to 173 kg CO_2-eq Mg^{-1} $season^{-1}$, less than half of that under continuous flooding (368 kg CO_2-eq $Mg^{-1}season^{-1}$), without compromising grain yield.

However, a critical trade-off of these practices is the enhanced soil aeration during drying phases, which stimulates microbial nitrification and denitrification, leading to increased N_2O emissions. For instance, N_2O emissions under AWD were 0.51 kg N_2O-N ha^{-1} compared to just 0.02 kg N_2O-N ha^{-1} under continuous flooding (Karki et al., 2022). While Liu et al. (2019) observed a 242% increase under MD. Other studies have reported N_2O fluxes ranging from 1.99 to 16.34 times higher than flooded controls (Verhoeven et al., 2018), though more moderate increases (~28.8%) have also been observed (Zhou et al., 2020; Wu et al., 2022). The consistently high N_2O emissions observed under AWD and MD underscore the need to address this trade-off to ensure their long-term sustainability.

Iron-based soil amendments offer a promising strategy to counteract the increase in N_2O emissions associated with water-saving irrigation practices. When applied to paddy soils, iron powder stimulates the growth of iron-reducing bacteria (IRB) such as *Geobacter* and *Anaeromyxobacter* (Masuda et al., 2021). This activity leads to the accumulation of ferrous iron (Fe^{2+}), which significantly lowers soil redox potential. These strong reducing conditions favor the complete reduction of N_2O to inert N_2 gas, thereby acting as a mechanism to mitigate emissions (Shen et al., 2022). In addition, iron powder promotes atmospheric nitrogen fixation, increasing ^{15}N incorporation and thereby reducing reliance on synthetic nitrogen fertilizers, an important step in minimizing excess reactive nitrogen in soils (Zhang et al., 2023).

Other forms of iron-based amendments further support this mitigation potential. For example, the incorporation of iron slag-derived silicate fertilizer has shown to reduce N_2O emissions by about 40% compared to controls (Galgo et al., 2024). Similarly, Fe-modified biochar suppresses nitrification by immobilizing NH_4^+ and reducing the abundance of ammonia-oxidizing bacteria (AOB), particularly *Nitrosospira* (Zhang et al., 2024). In Fe-biochar-treated soils, autotrophic nitrification rates decreased to 5.43 μg N g^{-1} d^{-1}, compared to 6.74 μg in the control and 9.38 μg with unmodified biochar. Additionally, Fe^{2+} plays a direct role in N transformations by serving as an electron donor. According to Wang et al. (2016), Fe^{2+} supplies 130.7% of the electron demand for NO_3^- reduction to N_2O, ensuring surplus electrons are available for full reduction to N_2, further minimizing emissions.

Integrating iron-based amendments with water-saving practices like AWD and MD offers a complementary strategy to mitigate N_2O emissions in rice paddies. Iron helps offset the unintended rise in N_2O caused by these practices, enabling more climate-resilient and sustainable rice cultivation.

2 N_2O production in rice fields

2.1 Role of rice plant

Plants, including rice, have traditionally been considered passive conduits for N_2O emissions, merely transporting N_2O produced by soil microorganisms to the atmosphere (Timilsina et al., 2022). However, a range of studies, including those using aseptically grown plants and ^{15}N isotope labelling, suggest that plants may also contribute directly to N_2O production through internal pathways. Timilsina et al. (2020) proposed a potential mechanism for N_2O formation in rice, involving a mitochondrial nitrate–nitrite–nitric oxide (NO_3^-–NO_2^-–NO) pathway that becomes active under hypoxic or anoxic conditions. In this model, NO_3^- is first reduced to nitrite (NO_2^-) in the cytoplasm by nitrate reductase ($NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O$), after which NO_2^- is transported to the mitochondria and further reduced to nitric oxide (NO) under low oxygen conditions ($NO_2^- + 2H^+ + e^- \rightarrow NO + H_2O$). Finally, NO is reduced to N_2O by the mitochondrial enzyme cytochrome c oxidase ($2NO + 2e^- + 2H^+ \rightarrow N_2O + H_2O$), particularly in its reduced form (**Fig. 1**). Although this pathway has not been conclusively verified in rice under natural field conditions, earlier studies observed increased N_2O emissions from rice plants following nitrate fertilization (Yu et al., 1997) and flooding (Yan et al., 2000), lending indirect support to the hypothesis that rice plants may be active contributors, not merely passive channels, in the N_2O emission process.

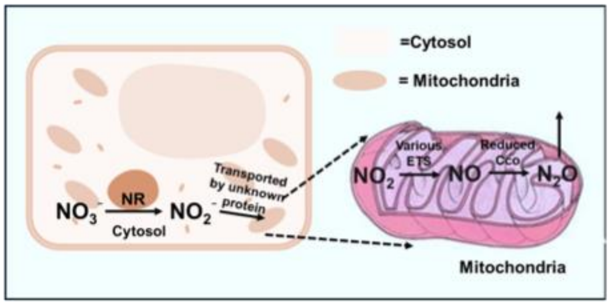

Figure 1. *The potential pathway of N_2O formation in rice plants under hypoxic conditions (NO = Nitric Oxide; NR = Nitrate reductase; ETS = Electron transport chains, and Cco = Cytochrome c oxidase). Modified from Timilsina et al. (2020).*

2.2 Role of soil in N_2O production

Soils are the major sources of N_2O, primarily through the processes of nitrification, denitrification, and coupled biotic-abiotic reactions. The following schematic diagram illustrates the major nitrogen transformations in soils and the pathways contributing to N_2O emissions (**Fig. 2**).

2.2.1 Nitrification pathway and N_2O production

This process is primarily mediated by chemoautotrophic nitrifying microorganisms (**Fig. 3**). Ammonia-oxidizing bacteria, such as *Nitrosomonas europaea*, carry out the oxidation of NH_4^+ to NO_2^-, while nitrite-oxidizing bacteria

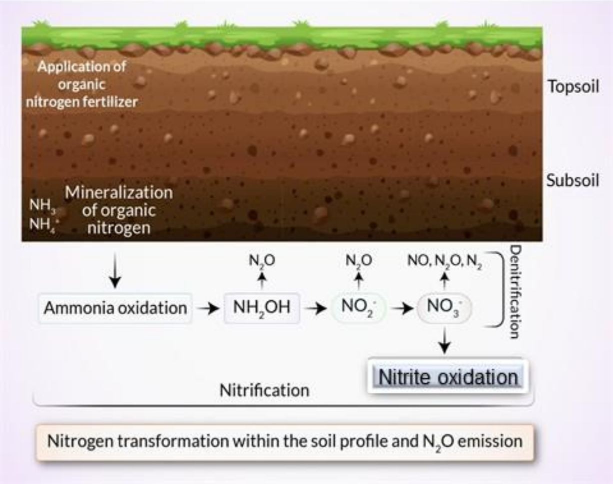

Figure 2. *Production of N_2O via microbial process (nitrification and denitrification). Modified from Abubaker (2012).*

(NOB), such as *Nitrobacter spp*., oxidize NO_2^- to NO_3^- (Aide, 2021). The overall chemical reactions are:

$$2NH_4^+ + 3O_2 = 2NO_2^- + 4H^+ + 2H_2O \text{ (by } \textit{Nitrosomonas}\text{)}$$

$$2NO_2^- + O_2 = 2NO_3^- \text{ (by } \textit{Nitrobacter}\text{)}$$

At the cellular level, the oxidation of ammonia (NH_3) to NO_2^- by canonical AOB is a two-step enzymatic process. First, ammonia monooxygenase (AMO) converts NH_3 to hydroxylamine (NH_2OH). Then, hydroxylamine oxidoreductase (HAO) oxidizes NH_2OH to NO_2^- (Monteiro et al., 2014; Stein and Klotz, 2016). However, recent studies show that NH_2OH is not just an intermediate but also a key precursor of NO and N_2O emissions. Under fluctuating redox conditions, HAO can partially oxidize NH_2OH to NO, which is subsequently reduced to N_2O by nitric oxide reductase (Nor), or converted abiotically to N_2O in the presence of oxygen (Caranto et al., 2016; Soler-Jofra et al., 2021). Additionally, under anaerobic conditions, cytochrome P460 (Cyt P460) has been shown to convert NH_2OH directly to N_2O via NO, functioning as a detoxification mechanism (Caranto et al., 2016). These alternative pathways highlight the central role of NH_2OH as a branching point between nitrification and N_2O production.

Ammonia oxidizers are now recognized as direct contributors to N_2O emissions through several mechanisms. One major pathway is nitrifier denitrification, wherein NO_2^-, produced during ammonia oxidation, is reduced to NO and then to N_2O by nitrite reductase and nitric oxide reductase, respectively (Zhu et al., 2013; Ju and Song, 2023; Liu et al., 2024). This process is particularly significant under low oxygen conditions (Kozlowski et al., 2014; Tan et al., 2024). Importantly, the NO_2^- generated in the nitrification pathway may also serve as a substrate for classical heterotrophic denitrifiers or be chemically or biologically reduced by Fe^{2+} in the presence of iron-oxidizing microorganisms, contributing further to N_2O production under fluctuating redox conditions (Kampschreur et al., 2011). These multiple fates of NO_2^- highlight its central role in linking nitrification, denitrification, and abiotic N_2O pathways in soils.

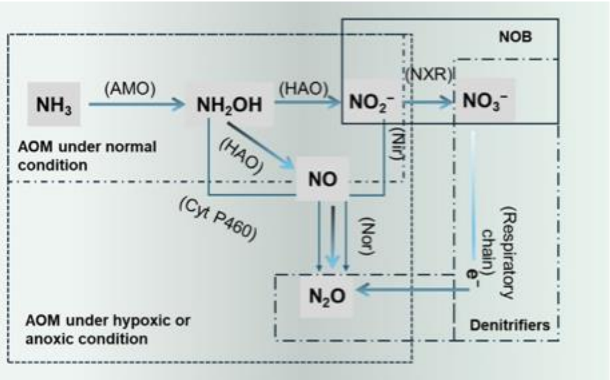

Figure 3. *N_2O production by bacterial activities. AMO = ammonium monooxygenase, HAO = hydroxylamine oxidoreductase, Cyt P460 = Cytochrome P460, Nir = nitrite reductase, Nor = NO reductase, NXR= Nitrite oxidoreductase, AOM= ammonia-oxidizing bacteria, and NOB= Nitrite-oxidizing bacteria. Sources: Caranto et al. (2016); Terada et al. (2017); Soler-Jofra et al. (2018); Stein (2019).*

2.2.2 Denitrification and N_2O production

Denitrification is a key microbial process in the nitrogen cycle, involving the reduction of NO_3^- or NO_2^- to gaseous forms of nitrogen, such as NO, N_2O, and N_2 under anaerobic conditions (Ranatunga et al., 2018). This process is primarily carried out by denitrifying bacteria, including species of *Pseudomonas* and *Alcaligenes*, which use NO_3^- and NO_2^- as terminal electron acceptors during respiration when oxygen is scarce (Firestone, 1982).

The denitrification pathway typically follows a sequential reduction process:

- Nitrate reduction: NO_3^- is reduced to NO_2^- by the enzyme nitrate reductase: $NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O$
- Nitrite reduction: NO_2^- is then reduced to NO by nitrite reductase: $NO_2^- + 2H^+ + e^- \rightarrow NO + H_2O$
- Nitric oxide reduction: NO is reduced to N_2O by nitric oxide reductase: $2NO + 2H^+ + 2e^- \rightarrow N_2O + H_2O$
- Nitrous oxide reduction: Finally, N_2O is reduced to N_2 by nitrous oxide reductase: $N_2O + 2H^+ + 2e^- \rightarrow N_2 + H_2O$
- The complete balanced equation for denitrification is: $2NO_3^- + 10\,e^- + 12\,H^+ \rightarrow N_2 + 6H_2O$

The extent of bacterial activity in denitrification is closely related to the water-filled pore space (WFPS) in the soil (see figure 6 in Bateman and Baggs, 2005). When WFPS exceeds 70%, the soil becomes increasingly anaerobic, favoring the activity of anaerobic microbes that contribute to N_2O emissions (Bateman and Baggs, 2005). Numerous studies have shown that N_2O emissions rise with increasing soil moisture, particularly when WFPS exceeds 60% (Wei et al., 2022; Liu et al., 2022; Oliveira et al., 2022). As WFPS increases, oxygen diffusion into the soil is restricted, leading to a larger proportion of anaerobic microsites, which are crucial for denitrification and N_2O production (Fairbairn et al., 2023; Schlüter et al., 2024). For example, Loick et al. (2021) and Bracken et al. (2021) identified 65% WFPS as a critical level above which N_2O emissions from grassland soils significantly increase. In rice fields, where the soil is often submerged, high WFPS creates an environment conducive to denitrification, making these fields significant sources of N_2O emissions.

3 Water saving irrigation management practices and N_2O production

Water-saving irrigation techniques such as AWD and MD have been promoted as sustainable solutions to reduce water use in rice cultivation. However, these practices often lead to increased emissions of N_2O, a potent greenhouse gas, due to enhanced soil aeration and nitrogen transformations. In contrast, continuous flooding (CF), the conventional irrigation practice, tends to emit lower N_2O levels owing to its stable anaerobic conditions, but it is water-intensive and unsustainable in water-scarce regions (Liang et al., 2022; Liao et al., 2023).

Studies indicate that while CF suppresses nitrification due to oxygen limitation, its consistently low redox potential favors the complete reduction of denitrification intermediates N_2O to N_2 (Yu et al., 2018). This effectively minimizes the release of N_2O, resulting in N_2O emissions ranging from 0.14–0.55 kg N_2O-N ha^{-1} $season^{-1}$ (Zou et al., 2007). Although CF serves as a reference for low N_2O emissions, it lacks water-saving benefits, underscoring the need for mitigation strategies in water-efficient practices such as AWD and MD.

3.1 Alternate wetting and drying

Alternate wetting and drying is a water-saving technology that has proven effective in rice cultivation, enabling farmers to reduce irrigation water consumption without compromising yield. It significantly enhances water use efficiency (WUE) while maintaining or even improving rice yields under suitable conditions (Soliman et al., 2024; Duong et al., 2024). The method involves alternating between flooded and non-flooded conditions, typically applying irrigation a few days after the disappearance of ponded water (Bwire et al., 2024), and is commonly implemented using a 'field water tube' to monitor soil water depth (**Fig. 4**).

Beyond water conservation, AWD is widely recognized as a primary strategy for mitigating CH_4 emissions, the dominant greenhouse gas in traditional submerged rice systems (Du et al., 2025). Chu et al. (2025) reported that the periodic drainage events introduce oxygen into the soil profile, which effectively suppresses the activity of methanogenic archaea (methanogens) that require strictly anaerobic conditions to produce methane. Simultaneously, the oxic conditions promote methanotrophy, the microbial oxidation of methane (Maurer et al., 2008). Consequently, AWD can reduce CH_4 emissions by ~53% compared to CF (Anapalli et al., 2023), substantially lowering the net GWP despite the trade-offs.

Despite its agronomic benefits and success in methane mitigation, AWD has been shown to increase N_2O emissions compared to CF. Wu et al. (2022) reported a 28.8% increase in N_2O emissions under AWD. This rise is primarily attributed to the alternating oxic and anoxic conditions that stimulate microbial nitrification during drying phases and denitrification during rewetting (Zhou et al., 2020; Cao et al., 2022). These redox fluctuations enhance microbial activity and nitrogen transformations, leading to increased N_2O production (Cai et al., 1997; Lagomarsino et al., 2016).

Fertilizer management strongly interacts with AWD. Nitrogen-rich basal fertilization increases substrate availability during drying, promoting nitrification, while rewetting enhances denitrification, both contributing to N_2O emissions (Oo et al., 2018; Qiu et al., 2022). Additionally, the mineralization of native soil nitrogen and physical release of trapped N_2O from soil microsites further elevate emissions (Flessa and Beese, 1995; Verhoeven et al., 2018). Studies have shown that N_2O peaks are influenced more by the quantity than frequency of drainage events, suggesting that shorter drying periods may mitigate emissions (Towprayoon et al., 2005).

Although both nitrification and denitrification contribute to N_2O emissions under AWD, denitrification is often the dominant pathway (Eckei et al., 2024). Sriphirom and Rossopa (2024) observed N_2O losses ranging from 11.8% to 15.0% of total gaseous nitrogen emissions under AWD. Moreover, the magnitude of emissions is affected by the timing of fertilization and drainage events, as well as the availability of labile carbon and soil mineral nitrogen (McSwiney and Robertson, 2005; Hoben et al., 2011; Kim et al., 2013; Pittelkow et al., 2013).

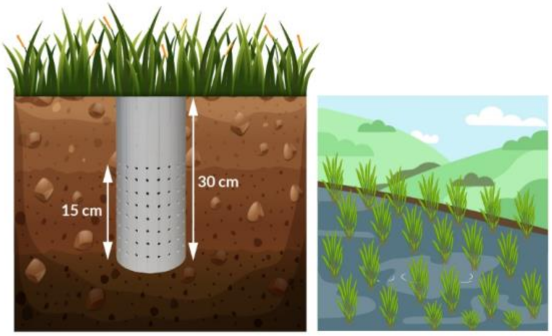

Figure 4. *Field water tube (Pani pipe). Modified from IRRI Rice Knowledge bank, (n.d.).*

While AWD effectively conserves water and can maintain yield, it introduces trade-offs in terms of elevated N_2O emissions. Its success depends on integrated nitrogen and irrigation management strategies that minimize emissions without compromising productivity.

3.2 Mid-season drainage

Mid-season drainage is a widely used water management practice in paddy fields, involving the temporary removal of surface water for 7 to 10 days before the maximum tillering stage (Ma et al., 2023). This brief drying period enhances soil aeration and has been shown to improve root development, soil health, and grain quality. Importantly, MD also reduces CH_4 emissions and limits arsenic accumulation in rice grains, all while maintaining grain yield (Wu et al., 2022; Dossou-Yovo et al., 2023; Perry et al., 2024). For example, Liu et al. (2019) reported that MD decreased CH_4 emissions by 52%, highlighting its strong potential for CH_4 mitigation. However, these environmental benefits come with trade-offs. MD has been consistently associated with a significant increase in N_2O emissions, which can undermine its overall climate mitigation benefit. Liu et al. (2019) found that MD increased N_2O emissions by 242% compared to continuous flooding. The shift to aerobic conditions during drainage stimulates microbial nitrification by AOB and supports coupled nitrification–denitrification in surface soil layers (Wu et al., 2023). As a result, N_2O emissions under MD can range from 1.99 to 16.34 times higher than those observed under continuous flooding (Verhoeven et al., 2018). On average, MD contributes an additional 0.248 kg N_2O-N ha^{-1} per season, accounting for approximately 3% of the seasonal global warming potential (GWP) (Perry et al., 2022).

These elevated emissions are further amplified by increased soil mineral nitrogen concentrations and enhanced availability of labile carbon, both of which result from accelerated organic matter mineralization under temporarily oxic conditions (La Hue et al., 2016). Additionally, the abundance of active nirS-type denitrifiers, particularly in acidic soils, plays a key role in enhancing denitrification-driven N_2O production during drainage events (Perry et al., 2022). The sharp redox potential (Eh) shifts that occur during drainage–reflooding cycles further intensify microbial activity, triggering episodic N_2O fluxes that typically peak shortly after drainage and decline after reflooding (Ussiri and Lal, 2013; Tariq et al., 2017).

Thus, while MD offers clear agronomic and environmental benefits—especially in terms of methane reduction and arsenic control—its potential to elevate N_2O emissions introduces a critical trade-off. To maximize MD's sustainability, integrated nitrogen and water management strategies are essential (Jeong et al., 2023). **Table 1 and Figure 5** summarize seasonal N_2O emissions under different irrigation regimes, such as AWD and MD, compared to CF, to contextualize their roles in N_2O dynamics in rice systems.

AWD and MD offer promising solutions for reducing water use and CH_4 emissions in rice systems, while maintaining or improving yields. However, these benefits are

Table 1. *N_2O and CH_4 emissions from rice paddies under different water management practices (kg N_2O-N ha^{-1} $season^{-1}$).*

Practice	N_2O emissions range (kg ha^{-1} $season^{-1}$)	CH_4 emission range (kg ha^{-1} $season^{-1}$)	References
Continuous flooding (CF)	0.14–0.55	29–75	Zou et al. (2007); Wang et al. (2011); Anapalli et al. (2023)
Alternate wetting & drying (AWD)	0.213–0.84	14–34	Gao et al. (2024); Liu et al. (2019)
Dry-direct-seeded rice (DDSR)	0.181–0.71	15–20	Li et al. (2019); Kaur et al. (2024)
System of rice intensification (SRI)	0.17–0.67	8.7–22.5	Jain et al. (2014); Abdulkadir et al. (2022)
Mid-season drainage (MSD)	0.20–0.73	14–36	Wang et al. (2016); Liu et al. (2019)

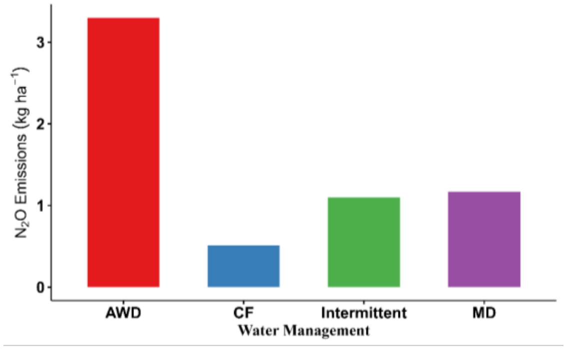

Figure 5. *Comparison of N_2O emissions from rice fields under different water management techniques. AWD = Alternate Wetting and Drying, CF = Continuous Flooding, MD = Mid-season Drainage. Source: Li et al. (2011); Kim et al. (2014); Chidthaisong et al. (2018); Karki et al. (2022).*

counterbalanced by elevated N_2O emissions. Compared to CF, which is effective in suppressing N_2O emissions but unsustainable in water-limited regions, AWD and MD show 2 to 8 times higher N_2O fluxes, making it essential to implement targeted mitigation strategies. Balancing productivity, water conservation, and climate impact remains critical for the success of sustainable rice intensification.

4 Iron-mediated nitrogen cycling in paddy soils

4.1 Iron-mediated biological nitrogen fixation

Biological nitrogen fixation (BNF) is an enzymatic process whereby atmospheric N_2 is converted into NH_3 by nitrogen-fixing bacteria using nitrogenase, under ambient temperature and pressure (De Bruijn, 2015). BNF is gaining increasing attention globally as a sustainable nitrogen input method because it does not require fossil fuel energy nor does it contribute to nitrogen pollution (Dai et al., 2021; Zhang et al., 2021). Besides synthetic nitrogen fertilizers, BNF is a primary nitrogen source in paddy soils (De Bruijn, 2015; Ladha et al., 2016).

Traditional approaches such as culturomics and PCR targeting the nitrogenase gene (nif) have identified diverse diazotrophs in paddy soils, including *Cyanobacteria*, *Firmicutes*, *Actinobacteria*, and several groups of *Proteobacteria* (Galhano et al., 2011; Shu et al., 2012; Wang et al., 2019). However, recent metagenomic and metatranscriptomic evidence shows that nif genes and transcripts are dominated by *Anaeromyxobacter* and *Geobacter* (Masuda et al., 2017), two *Deltaproteobacteria* that are also the major iron-reducing bacteria in flooded soils (Hori et al., 2015). Their dual capacity for iron reduction and nitrogen fixation positions them as central players in the nitrogen cycling of paddy soils.

Experimental studies strengthen this interpretation. In sterile microcosms, *Anaeromyxobacter* strains were shown to fix atmospheric N_2 (Masuda et al., 2020). Field experiments further demonstrate that Fe amendments (e.g., Fe_2O_3) enhance the activity of these IRB by providing Fe^{3+} as an electron acceptor during anaerobic respiration, thereby stimulating nitrogenase-mediated N_2 fixation (Masuda et al., 2021). Complementary ^{15}N-IRMS and ^{15}N-DNA-SIP analyses confirm greater atmospheric ^{15}N incorporation in iron-powder–amended soils, indicating an increase in biologically fixed nitrogen (Zhang et al., 2023). Iron amendment via IP promotes the growth and activity of iron-reducing bacteria, enhancing biological nitrogen fixation in paddy soils (**Fig. 6**). This process increases nitrogen availability for rice, reduces nitrogen losses, and may mitigate N_2O emissions.

4.2 Suppression of autotrophic nitrification by Fe amendment

Iron amendments play an important role in regulating N transformations in paddy soils, particularly through their effects on autotrophic nitrification, a major source of N_2O emissions. Oxidized forms of iron, especially Fe(III) oxides, can immobilize NH_4^+ and limit substrate availability for nitrifiers, thereby suppressing nitrification activity (Jiang et al., 2015; Zhu-Barker et al., 2015).

Recent work highlights the strong mitigation potential of iron-modified amendments. For example, Zhang et al. (2024) found that Fe-modified biochar reduced nitrification by 42% compared with unmodified biochar, largely due to lower NH_4^+ availability and inhibited growth of AOB, including *Nitrosospira* (see figure 4 in Zhang et al., 2024). Fe

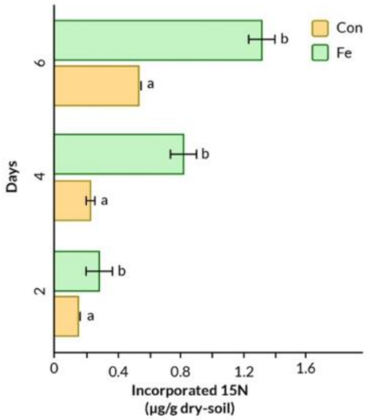

Figure 6. *The amount of ^{15}N incorporated in iron-applied (Fe) and non-applied native (Con) plot paddy soils. Adapted from Zhang et al. (2023).*

amendment also shifted the nitrifying community toward ammonia-oxidizing archaea (AOA), which are generally associated with lower N_2O production (Hink et al., 2017; Zuo et al., 2020). These effects arise from both chemical and biological interactions: Fe oxides adsorb NH_4^+ (Huang et al., 2016), alter microbial gene expression, and restructure nitrifier populations (Wu et al., 2020). The response can be particularly strong in neutral to alkaline soils, where AOB dominate nitrification (Jia and Conrad, 2009). However, the influence of iron is not uniform across soil types. In acidic soils, some studies report that iron oxides may stimulate nitrification and N_2O emissions by promoting ammonium mineralization or shifting microbial communities toward nitrifiers (Sun et al., 2018). Zuo et al. (2020), for instance, observed that goethite increased ammonia-oxidizing archaea abundance in both acidic and alkaline soils, though its impact on N_2O varied with soil conditions.

These findings emphasize that the effectiveness of iron-based amendments in suppressing nitrification, and thus mitigating N_2O emissions, depends strongly on soil pH, iron speciation, and microbial community dynamics. While Fe-modified materials show substantial potential under favorable conditions, their performance must be evaluated carefully across different soils and management practices.

4.3 Denitrification mediated by ferrous iron

Iron, particularly Fe^{2+}, plays a crucial role in regulating N_2O emissions from paddy soils by serving as an electron donor in the denitrification process (Carlson et al., 2013; Zhu et al., 2013). Fe^{2+} oxidation coupled with nitrate and nitrite reduction can lower N_2O emissions by facilitating its further reduction to N_2. Wang et al. (2016) reported that Fe^{2+} contributed 16.2% and 32.9% of the total electrons for denitrification in low- and high-Fe^{2+} soils, respectively, with the electron contribution exceeding the demand for N_2O production (130.7%) in high-Fe^{2+} soils, suggesting potential for complete N_2O reduction to N_2.

The process is energetically favorable, particularly under neutral pH conditions, where Fe^{2+} can be oxidized to Fe^{3+} while contributing electrons to the reduction of nitrogen oxides (Klueglein and Kappler, 2013; Melton et al., 2014). This interaction can be described by the following chemical reactions:

$$\text{Fe}^{2+}\text{ oxidation: } Fe^{2+} \rightarrow Fe^{3+} + e^-$$

$$\text{Nitrate reduction: } NO_3^- + 2e^- + 2H^+ \rightarrow NO_2^- + H_2O$$

$$\text{Nitrite reduction: } NO_2^- + 2e^- + 3H^+ \rightarrow 0.5N_2O + 1.5H_2O$$

$$\text{Further reduction of } N_2O\text{: } 0.5N_2O + e^- + H^+ \rightarrow 0.5N_2 + 0.5H_2O$$

In this sequence, Fe^{2+} provides the necessary electrons to drive the reduction of N_2O to N_2, thereby mitigating N_2O emissions. The Nitrate-dependent Fe(II) oxidation process plays a critical role in linking the iron and nitrogen cycles in paddy soils (Yang et al., 2024a). In this process, Fe^{2+} is oxidized to Fe^{3+}, while NO_3^- and NO_2^- are concurrently reduced to N_2O or N_2 through a coupled redox reaction. This redox interaction significantly influences the production and emission of N_2O (Yang et al., 2024b).

Paddy soils naturally experience cyclical wetting and drying, which drives dynamic shifts in iron redox states. During flooding, reducing conditions favor the accumulation of Fe^{2+}, while during drying or drainage events, oxidizing conditions promote the conversion of Fe^{2+} back to Fe^{3+} (Kögel-Knabner et al., 2010). For example, during the late rice season, drainage oxidizes Fe^{2+} to Fe^{3+}, releasing electrons that facilitate the complete reduction of nitrogen compounds to N_2, thereby promoting complete denitrification (Wang et al., 2016; Wang et al., 2020).

In addition to redox conditions, biological and chemical factors strongly modulate Fe–N interactions. For instance, wetland *archaebacteria* can reduce Fe^{3+} to Fe^{2+}, thereby influencing the availability of electron donors and affecting N_2O dynamics (Zhang et al., 2021). Moreover, organic carbon (OC) also mediates iron cycling. It can reduce Fe^{3+} via the reaction:

$$CH_2O + 2Fe^{3+} + 2OH^- \rightarrow 2Fe^{2+} + H_2O + 2CO_2$$

Deng et al. (2020) demonstrated that moderate levels of OC enhanced N_2O reduction in a Fe^0-based autotrophic denitrification system, suggesting that OC inputs can synergize with iron-mediated processes. These findings highlight the potential of iron amendments to mitigate N_2O emissions in rice systems. However, the effectiveness of such strategies depends on multiple interacting variables, including redox dynamics, microbial activity, and organic carbon availability. Therefore, further research is essential to determine the optimal form, dosage, and timing of iron application to ensure maximum benefit while avoiding unintended environmental impacts.

5 Integrating iron amendment with water-saving irrigation strategies

Integrating soil amendments with irrigation strategies is gaining attention as a way to reduce GHG emissions from rice paddies. In particular, the combination of IA and water-saving irrigation practices such as AWD or MD shows promise for simultaneously improving environmental performance and maintaining rice yield. AWD has been widely recognized for significantly reducing CH_4 emissions compared to CF, with average reductions of around 73%. Karki et al. (2022) reported that the yield-scaled GWP under AWD was 173 kg CO_2-eq Mg^{-1} $season^{-1}$, less than half of that under CF (368 kg CO_2-eq Mg^{-1} $season^{-1}$), with no significant change in grain yield. However, a key drawback of AWD and MD is their tendency to increase N_2O emissions. Karki et al. (2022) observed that N_2O emissions under AWD were 0.51 kg N_2O-N ha^{-1} compared to just 0.02 kg N_2O-N ha^{-1} under CF, a more than 25-fold increase. Similarly, Liu et al. (2019) reported a 242% increase in N_2O under MD, and Verhoeven et al. (2018) recorded N_2O fluxes that were 1.99 to 16.34 times higher than under CF. In contrast, other studies have reported more moderate increases; for instance, Zhou et al. (2020) and Wu et al. (2022) found an average increase of 28.8% under AWD. These variations underscore the influence of site-specific factors and the need for optimized water and nitrogen management practices. Given N_2O's global warming potential is approximately 298 times that of CO_2, mitigating its emissions is essential to realizing the full climate benefits of AWD or MD.

IA helps address this trade-off by stimulating nitrogen fixation and suppressing nitrification and denitrification processes that generate N_2O. IP enhances the activity of iron-reducing bacteria such as *Anaeromyxobacter* and *Geobacter*, leading to higher atmospheric ^{15}N incorporation and reduced dependence on nitrogen fertilizers (Masuda et al., 2021; Zhang et al., 2023). This decreases the nitrogen available for microbial N_2O production. Iron slag-based silicate fertilizer incorporation has been shown to reduce N_2O emissions by approximately 40% compared to control treatments (Galgo et al., 2024), further supporting the role of iron-based amendments in N_2O mitigation. In parallel, the application of Fe-modified biochar has been shown to inhibit nitrification by immobilizing NH_4^+ and suppressing AOB, especially *Nitrosospira* (Zhang et al., 2024). The gross rate of autotrophic nitrification was reduced to 5.43 μg N g^{-1} d^{-1} in Fe-biochar-amended soil, compared to 6.74 μg N g^{-1} d^{-1} in the control and 9.38 μg N g^{-1} d^{-1} in the unmodified biochar treatment. In addition, Fe^{2+} has been reported to supply 130.7% of the electron demand for NO_3^- reduction to N_2O, indicating that excess electrons are available to further reduce N_2O to N_2, thereby decreasing its emission (Wang et al., 2016).

The synergy between IP and water-saving irrigation thus provides both environmental and agronomic benefits. By reducing the need for nitrogen inputs and minimizing CH_4 and N_2O emissions, this approach improves nitrogen use efficiency and lowers GHG emissions. Moreover, it reduces the risk of nitrogen leaching and helps prevent the accumulation of harmful elements often associated with long-term flooding. Together, these practices represent a climate-smart solution for sustainable rice cultivation under changing environmental conditions.

6 Conclusion

Iron-based amendments offer a promising solution to the trade-off created by water-saving irrigation practices such as AWD and MD, which, despite reducing CH_4 emissions by up to 27.6% and lowering irrigation water demand by 15–30%, often increase N_2O emissions by 28.8% to more than 16-fold. Iron amendments enhance nitrogen retention and stabilize soil redox conditions by stimulating iron-reducing bacteria, generating Fe^{2+}, and limiting nitrate accumulation. These processes suppress both nitrification and denitrification pathways responsible for N_2O formation. Additionally, Fe^{2+} can abiotically reduce N_2O to N_2, while Fe-modified biochar further decreases nitrification rates, e.g., from 9.38 to 5.43 μg N g^{-1} d^{-1}, providing multiple complementary mechanisms to curb N_2O emissions during aerobic phases. When integrated with AWD or MD, iron amendments may mitigate N_2O emissions without compromising rice productivity, and studies already demonstrate reductions of around 40% under certain iron-based fertilizers. This synergy suggests a strong potential for developing climate-resilient, low-emission rice systems that maintain the benefits of water-saving irrigation while minimizing greenhouse gas trade-offs. However, long-term and field-scale evaluations are needed to confirm these advantages under diverse agroecosystems and to understand the residual behavior of applied iron. Optimizing amendment type, rate, and timing will also be critical to ensure agronomic efficiency and environmental safety. Overall, combining iron amendments with water-saving irrigation represents a viable and scalable strategy for addressing the N_2O trade-off in rice production—supporting global goals for climate mitigation and food security.

7 Data availability statement

All data generated or analyzed during this study are included in the manuscript. The raw data are available from the corresponding author upon reasonable request.

8 Ethical statements

There are no ethical issues with the manuscript.

9 Conflict of interest

The authors affirm that publishing this manuscript does not put them in a conflict of interest.

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11 Author contributions

Md Roconuzzaman Nasim: Conceptualization, methodology, software, data acquisition, analysis, visualization, and writing – original draft. Joy Sarker: Data curation, writing – original draft, and writing – review and editing. Khadija Khatun Keya: Writing – review and editing. Md. Hasibul Hasan: Writing – review and editing, software, and visualization. Sharmin Akter: Writing – review and editing. Md. Rafiqul Islam: Conceptualization, validation, investigation, resources, writing – review and editing, and supervision. All authors read and approved the final version of the manuscript for its publication.

12 Copyright statement

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