Nitrification inhibitors for controlling methane emission from submerged rice soils

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Submerged rice fields are considered an important source of atmospheric methane and attention is focussed on mitigating methane emissions from wetland rice soils. We assess here the prospects of reducing methane emission from flooded rice soils by using nitrification inhibitors. Nitrification inhibitors retard nitrification, affect nitrogen transformations other than nitrification, and reduce nitrous oxide production in upland soils. The review of recent literature indicates that nitrification inhibitors have the ability to inhibit or retard methane production and emission in submerged rice soils. Various compounds or materials evaluated show that they have a wide range in their efficacy for mitigating methane emission from submerged soils. Although the mechanisms involved in reducing methane production by nitrification inhibitors are not fully understood, initial observations would suggest that in addition to decreasing the population of methanogens, some nitrification inhibitors act as oxidant and their application to flooded soil system maintain soil redox potential at relatively higher levels. There is an obvious need for a systematic approach to research for evaluating compounds and materials for mitigating the emission of methane and other radiatively-active gases, such as nitrous oxide and carbon dioxide from lowland rice soils.

THE involvement of greenhouse gases, carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and chlorofluorocarbons (CFCs) in global warming has focused attention on the ways to mitigate their emission to the atmosphere. Lowland rice fields are considered as important source of atmospheric methane and considerable attention is given to mitigating methane emissions from flooded rice[1,2]. Although the atmospheric concentration of methane is far lower than that of carbon dioxide, methane has high thermal sorbing capability and its contribution to global warming is greater than its concentration would suggest[3,4]. In fact, on a mole basis, considering the decay time of radiatively active gases in the atmosphere, methane has five times more infrared sorbing capability than carbon dioxide[3].

Methane is produced as the terminal step of the anaerobic decomposition of organic matter in flooded soils. Methanogenic bacteria exclusively produce methane in the strict absence of free oxygen at redox potentials of less than –150 mV[5]. In wetland soils, methane is produced by decarboxylation of acetate and by reduction of carbon dioxide[6]. The production of methane during decomposition of organic matter under anaerobic conditions is controlled by the flow of carbon and electrons to the microbial population of methanogens. In addition, the thermodynamic constraints of the *in-situ* reactions involved and changes in the composition of the microbial community affect methane production[7]. Methane emission to the atmosphere is the net difference between methane production and oxidation controlled by methanogens, methanotrophs and ammonium oxidizers.

Recent reviews[1,2,8] have covered the aspects related to methane production and its fluxes from lowland rice fields and crop and water management strategies for mitigating methane emissions from lowland rice fields. No doubt, land and water management practices can be used for reducing methane production and emission from lowland rice soils but the influence of these management practices on crop productivity need to be considered when evaluating and implementing such practices. Also, application, especially of water management practices may require a good water control that may not always be practically feasible.

The use of chemical agents (compounds or materials) that can inhibit or retard methane production and emission appear attractive for mitigating methane emission from lowland rice fields. The compounds or materials proposed for mitigating methane emission should be effective at reasonable rates of application and should be safe and without any deleterious side effects on soil microbial populations.

Nitrification and nitrification inhibitors: general concepts

Nitrification is generally used to mean biological oxidation of ammonium to nitrate via nitrite effected, respectively by *Nitrosomonas* and *Nitrobacter* species of nitrifying bacteria, although nitrification inhibitors are defined as compounds or materials that specifically inhibit or retard the oxidation of ammonium to nitrite without affecting the subsequent oxidation of nitrite to nitrate[9]. Nitrification inhibitors have been used with advantage for improv-

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ing crop production and crop quality and for the control of nitrate pollution of surface and ground waters[10–12]. Nitrification inhibitors improve crop productivity by reducing the loss of nitrate via leaching or denitrification[9,10]. These chemical agents improve crop quality by improving availability of nitrogen and by reducing accumulation of nitrate in plants[11]. At recommended rates, nitrification inhibitors do not generally affect beneficial soil microorganisms[12].

Nitrification inhibitors not only influence nitrification in soil, but also affect physical, chemical and biological processes affecting N transformations, other than nitrification, such as the transport, movement and persistence of N in the soil and its gaseous loss to the atmosphere[9,13] (Table 1). Several workers have reported that the addition of nitrification inhibitors, such as nitrapyrin and acetylene with urea and ammonium containing fertilizers reduces nitrous oxide production in upland soils[9,14–16]. Banerjee and Mosier[17] demonstrated that encapsulated calcium carbide is a slow-release source of acetylene that inhibits nitrification and reduces nitrous oxide fluxes in flooded soils. Acetylene also has been reported to inhibit methane production[18].

There are reports that nitrification inhibitors can also reduce methane emission from lowland rice. Although methane emission from rice fields does not contribute to N fertilizer loss, methane emission is of concern because methane is an important greenhouse (radiatively active) gas. It was thought important to assess recent literature on the use of nitrification inhibitors for controlling methane emissions from lowland rice soils. If compounds or materials employed for retarding nitrification and associated nitrous oxide emission also reduce methane emission from soils, it would help not only in improving the efficiency of N but also in controlling global warming. This paper assesses the prospects of mitigating methane emission from lowland rice soils by employing nitrification inhibitors and also examines the need for future research.

Nitrification inhibitors and methane emission from flooded rice soils

Following research on the effects of nitrification inhibitors on nitrification and nitrous oxide production in upland soils, nitrification inhibitors have been evaluated for mitigating methane emission from flooded lowland rice soils. For example, Bronson and Mosier[19] evaluated the effects of nitrification inhibitors on emissions of N_2, CO_2, N_2O and CH_4 from flooded pots in a greenhouse study. It was found that nitrification inhibitor, encapsulated calcium carbide, showed a strong mitigating effect on emissions of N_2 and CH_4. Nitrous oxide fluxes were also reduced by calcium carbide, but the magnitude of losses with urea alone were very small in flooded rice. Carbon dioxide emissions were lower with encapsulated calcium carbide than without it. The effect of the N rate on methane emissions was variable over the 30 days of study. From the results obtained, it was concluded that encapsulated calcium carbide appears to be an effective tool in reducing emissions of the radiatively active gases, nitrous oxide and methane[19].

In a micro-plot study in the field, Keerthisinghe *et al.*[20] found that nitrapyrin and acetylene nitrification inhibitors significantly reduced methane emission in flooded rice. The lowest methane emission rates were observed in the wax-coated calcium carbide treatment. Wax-coated calcium carbide acted as a slow release source of acetylene and produced a sustained effect in reducing methane emissions. Application of nitrapyrin and wax-coated calcium carbide reduced methane emission from 15.4 g CH_4 ha^{-1} d^{-1} in the control to 5.8 and 2.8 g CH_4 ha^{-1} d^{-1}, respectively. The reduction in methane emission by calcium carbide was a direct result of slow release of acetylene, which inhibits production of methanogenic bacteria[18]. The mechanism involved for reducing methane emission by nitrapyrin was not established. Acetylene is also a potent inhibitor of nitrification in aerobic soils[21,22].

It was also found that nitrapyrin did not significantly affect nitrous oxide emission, while calcium carbide did. These results on the effect of nitrapyrin on nitrous oxide production in flooded soil[20] contrast with those from upland soils[14]. These results further suggest that while nitrapyrin and other nitrification inhibitors reduce nitrous oxide production associated with nitrification in upland soils, they do not affect nitrous oxide production via denitrification of nitrates in flooded soils.

Kumaraswamy *et al.*[23] conducted laboratory and field experiments to evaluate the effects of carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl N-methylcarbamate), a carbamate insecticide, on methane production and emission. In the field, application of commercial formulation of the insecticide at 2 and 12 kg active ingredient (a.i.) ha^{-1} reduced methane emissions from flooded rice. In laboratory experiments, the application of carbofuran at 5 and 10 mg kg^{-1} soil to the flooded soil inhibited methane production relative to control (no carbofuran).

Table 1. Physical, chemical and biological processes of nitrogen transformations, other than nitrification, affected by nitrification inhibitors in the soil (adapted from ref. 9)

Physical and chemical processes
Nitrogen transport and movement
Ammonium fixation and release
Ammonia volatilization
Biological processes
Mineralization and immobilization
Denitrification
Nitrous oxide production
Urea hydrolysis

Table 2. Effects of commercial formulation of carbofuran on methane emission from flooded rice fields. Carbofuran was broadcast applied on the 47th after transplanting (panicle initiation rice plant growth stage). The values in parentheses are the days after transplanting of rice (adapted from ref. 23)

	Methane flux (mmol m^{-2} h^{-1}) at days after carbofuran application[a]					
Treatment	4 (51)	9 (56)	14 (61)	21 (68)	26 (73)	30 (77)
No carbofuran	1.51a	1.60a	1.59a	0.40a	0.31a	0.26a
Carbofuran at 2 kg a.i. ha^{-1}	1.30b	0.47a	0.79b	0.16b	0.17b	0.14b
Carbofuran at 12 kg a.i. ha^{-1}	0.22c	0.87a	0.89b	0.31a	0.22b	0.16b

[a]In a column, means followed by a common letter are not significantly different at $P < 0.05$ by Duncan's multiple range test.

Carbofuran increased the oxidation of methane when applied at higher rates, but inhibited methane production at lower rates of application. The ability of carbofuran to inhibit methane production at low rates of application was evident from the results that showed that the insecticide caused a distinct reduction in methane flux at field rate application (2 kg a.i. ha^{-1}). In the laboratory experiment, carbofuran application had a positive effect on the autotrophic ammonium oxidizer population. The insecticide application stimulated methane oxidizers when applied at low concentrations[23]. Some results on the effect of carbofuran application on methane fluxes from flooded rice in the field are given in Table 2. Nitrification inhibitors are known for inhibiting methane oxidation and reducing the methane oxidizing population[24]. Also, autotrophic ammonium oxidizers have been implicated in the oxidation of methane[25]. Carbofuran has been reported to retard the nitrification of ammonium N in soils under aerobic conditions[26].

Bharati *et al.*[27] conducted laboratory incubation experiment to evaluate the effects of addition of six nitrification inhibitors on methane production in an alluvial soil under flooded condition. The inhibition of methane production followed the order: sodium azide > dicyandiamide (DCD) > pyridine > aminopurine > ammonium thiosulfate > thiourea. It was observed that the inhibition of methane production in DCD-amended soil treatments was related to a high redox potential, low pH, low ferrous iron concentration and lower availability of readily mineralizable C, and a lower population of methanogenic bacteria and their decreased activity. Application of urea at a rate of 40 mg N kg^{-1} soil partially alleviated the inhibitory effect of DCD on methane production. It was concluded that nitrification inhibitors have the ability to differentially regulate methane production in flooded soil[27].

Perspectives

Methane emission from flooded rice can be mitigated by decreasing methane production, increasing oxidation of methane produced or by reducing the transport of methane through rice plants. Nitrification inhibitors in general affect methane emission by influencing methane production and methane oxidation. The review of recent literature indicates that nitrification inhibitors have the ability to reduce methane production and emission from lowland rice soils. Research on the evaluation of a number of compounds or materials indicate that nitrification inhibitors have a wide range in their efficacy to reduce methane production or emission from flooded rice soils. The mechanisms involved in mitigating methane production and emission by nitrification inhibitors are not fully understood, but studies made with some nitrification inhibitors would suggest that in addition to decreasing the populations of methanogens, they also act as oxidants and are able to maintain the redox potential of flooded soil systems at relatively higher values compared to the control (without addition of nitrification inhibitor). Nitrification inhibitors reduce methane emission by reducing methane production and/or by oxidation of methane produced.

Nitrification inhibitors affect ammonium oxidation through their effects on ammonia monoxygenase enzyme that has a very broad substrate range and can account for the inhibitory effect of many compounds on the enzyme[28]. It is postulated that nitrification inhibitors control methane emission through methane oxidation by influencing methane monoxygenase enzyme. Moreover, the presence and concentration of ammonium in the medium at different stages of the methanogens population dynamics has been reported to have differential effects on methane oxidation and emission[29–32]. This finding has crucial implications for control of methane emissions because there is preferential accumulation of ammonium following inhibition of nitrification of ammonium to nitrite in soils[9]. There is need for further research on the role of nitrification inhibitors on control of methane oxidation by manipulating ammonium concentration in the medium at specific growth stages of the methanogens.

The results discussed also offer encouragement for future research on the use of nitrification inhibitors for reducing methane emission from flooded rice. There is an obvious need for a systematic approach to the research for evaluating compounds or materials proposed as inhibitors or retarders of nitrification for mitigating methane emission from submerged rice soils. There is also need for establishing the mechanisms involved in reducing methane emissions by various compounds or materials. Such research would facilitate identification and synthesis of compounds for mitigating methane emission from flooded rice

It is emphasized that for the future research compounds or materials with nitrification inhibitory activity should be evaluated for reducing not only methane production and emission, but also for their effectiveness in reducing the emission of other radiatively active gases namely, nitrous oxide and carbon dioxide from flooded rice. The use of nitrification inhibitors provides an alternative approach to reduce the emission of greenhouse gases such as nitrous oxide and methane. The use of nitrification inhibitors in conjunction with other approaches based on soil, water and ecosystem management is suggested for reducing the emission of methane[33,34].

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