The Journal of Animal & Plant Sciences, 24(2): 2014, Page: 354-361
ISSN: 1018-7081

REVIEW PAPER

ROLE OF ENCAPSULATED CALCIUM CARBIDE IN NITROGEN ECONOMY, GROWTH AND YIELD OF CROPS: A REVIEW

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ABSTRACT

Various types of nitrogen losses whither to the atmosphere or to lower soil layers, result in low fertilizer N-use efficiency of crop plants.Ammonia volatilization is the major source of N-loss particularly when fertilizers are broadcasted on surface of alkaline soils. Nitrogen loss as NH_3 can be decreased by alternative methods to broadcast like placement and side dressing. However, incorporation increases the soil-fertilizer contact and results in an increase in nitrification.Excess amount of nitrate formed during nitrification losses through leaching or denitrification. The loss of incorporated fertilizer nitrogen can be reduced by nitrification inhibition.A number of commercially available compounds have been reported as nitrification inhibitors (NI,s) but their effectiveness is limited due to one or the other reasons. Acetylene is another NI and owing to gaseous nature its application and maintenance in soil is difficult. To solve this problem, a suggested approach is to encapsulate calcium carbide with some hydrophobic materialto slow down spontaneous reaction of CaC_2 with water and produce acetylene in soil. Encapsulated calcium carbide (ECC) application to soil inhibits nitrification, reduces nitrate leaching, nitrous oxide emissions and improves nitrogen uptake in favor of nitrogen use efficiency of crop plants. Type of encapsulation, and time, rate and depth of application of ECC significantly affect the efficacy of the approach. Another aspect of ECC released acetylene is its biological reduction to ethylene,a gaseous plant hormone which also has remarkable effects on plant growth. In this article various aspects of ECC application in crop production are discussed and research gaps are pointed out.

Key words: nitrification inhibition, encapsulated calcium carbide, acetylene, ethylene, nitrate leaching, denitrification

Why nitrification inhibition? Amongst the nutrients, nitrogen (N) is most limiting to growth and yield parameters of a crop. Its deficiency is overcome by the application of nitrogenous fertilizers which are not used efficiently by plants due to losses through various pathways (Fageria and Baligar, 2005). Ammonia volatilization is the major loss of N when fertilizers are broadcasted (Wang *et al.*, 2004) over the soil with high pH (Zhenghu and Honglang, 2000). Ammonia loss can be reduced by applying N fertilizer under the soil surface instead of broadcasting. In the form of a layer of soil, incorporation of fertilizer provides a physical barrier to volatilization (Thompson and Meisinger, 2002). However, entrapment of ammoniaresults in its close contact with soil and rapid nitrification (Azam and Farooq, 2003).

Nitrification is the biological oxidation of ammonium to nitrate via nitrite by Nitrosomonas and Nitrobacter species of bacteria (Grunditz and Dalhammar, 2001). Being having negative charge, nitrate does not stick to exchange sites. It leaches down to underground water (Köhler *et al*., 2006) or undergoes denitrification to form nitrogen oxides. These oxides emit to the atmosphere (Azam *et al*., 2002). Nitrate leaching and denitrification not only results in loss of costly fertilizer but also cause environmental pollution. Underground water with high nitrate concentrations, on drinking causes blue baby syndrome (methemoglobinemia), a condition which limits blood hemoglobin to carry oxygen to body cells (Fewtrell, 2004). On the other hand nitrous oxide, a product of denitrification, is a greenhouse gas (Robertson *et al*., 2000) and involved inozone depletion in troposphere and stratosphere (Ravishankara *et al*., 2009).

High rates of nitrification also results in nitrate accumulation in soil more than that of ammonium. This affects the choice of crop plants for nitrogen nutrition (Azam and Farooq, 2003). Although plants can uptake both nitrate and ammonium but most of them have preference for one or the other nitrogen form. It is now a proven fact that a large number of plant species grow better in mixed nitrate and ammonium nutrition than either form alone (Ali *et al*., 2001).

It is thus desirable to inhibit nitrification of fertilizer-N, incorporated to control ammonia volatilization, to reduce nitrogen losses through denitrification and nitrate leaching (Majumdar *et al*., 2000). It would also helpful to maintain a mixture of nitrate-N and ammonium-N in soil in favor of nitrogen use efficiency of crop plants (Azam and Farooq, 2003).

Nitrification inhibitors – at a glance: A number of compounds like dicyandiamide (DCD), nitrapyrin and 3, 4-dimethylpyrazole phosphate (DMPP) have been reported to inhibit the nitrification process in soils (Zerulla *et al*., 2001; Gioacchini *et al*., 2002; Majumdar *et al*., 2002; Irigoyen *et al*., 2003) andreduce nitrous oxide emissions and nitrate leaching (Zaman and Blennerhassett, 2010). There are a number of constraints in using these nitrification inhibitors (NI) in agriculture. For instance, according to Slangen and Kerkhoff (1984 cited by Freney *et al*., 2000) nitrapyrin, in some cases, is not so effective because of its unavailability from the system due to sorption on soil particles, molecular breakdown and volatilization. On the other hand DCD is sensitive to soil temperature. Its stability gradually decreased with an increase in temperature. At 8°C its half-life was about 111 to 116 days which was decreased sharply to 18-25 days at 20°C (Di and Cameron, 2004) A second constraint in application of DCD as NI is its solubility in water, which results in leaching and its separation from the fertilizer molecules (Shepherd *et al*., 2012).

Acetylene is another NI (Offre *et al*., 2009). Different acetylene concentrations are required for nitrification inhibition in different soils. For instance, acetylene concentration which was sufficient to inhibit nitrification in redoxic Luvisol did not properly retard the process in hypercalcareous Rendosol at water potentials -3.5 MPa (Garrido *et al*., 2000).

Although it is a good NI but owing to its gaseous nature it is problematic to apply and maintain acetylene at required partial pressures in soils. Researchers tried a number of non-gaseous acetylene releasing compounds in soil and declared2-ethynylpyridine and phenylacetylene as reliable sources of the gas for nitrification inhibition. Ferny *et al*. (1993) confirmed in a field experiment that these two compounds are effective in inhibiting nitrification of fertilizer N applied before the sowing of cotton. However, these compounds are of limited practical utilization in agriculture due to their high cost.

The second approach is to encapsulate calcium carbide with some hydrophobic material to slow its reaction with water [$CaC_2 + H_2O \rightarrow C_2H_2 + Ca(OH)_2$], and produce acetylene *in situ* in soil.

Encapsulation of calcium carbide: The word encapsulation is used here to express all types of coatings, filling to capsules and frame-up of calcium carbide particles in polyethylene matrix. Calcium carbide is a common ripening material (Vrebalov *et al*., 2002). It reacts spontaneously with water and produces acetylene which can be used for nitrification inhibition. If applied to soil without encapsulation, calcium carbide rapidly reacts with surplus soil moistureand converted into acetylene and calcium hydroxide. This abundant supply of the gas for few minutes does not maintain a required partial pressure of acetylene for reasonable period of time to inhibit nitrification.To slow down the reaction, particles of CaC_2 are encapsulated with some hydrophobic material to limit the entry of water to CaC_2. Initially the particles of calcium carbide were coated with waxes (Banerjee and Moiser, 1989). Later on a number of other hydrophobic materials were tried in CaC_2encapsulations. These materials include different types of waxes like beeswax, paraffin wax; gelatin medical capsules, black enamel paint and polyethylene (Mahmood *et al*., 2010).

Not only the type of hydrophobic material, but also the particle size of calcium carbide particles, going to beencapsulated, is important for acetylene and ethylene flux. Mostly 2-4 mm diameter particles of calcium carbide are coated, whereas in capsules and in polyethylene matrices, CaC_2 is used in powder form. Due to high cohesiveness of polyethylene, some sparingly water soluble materials like calcium carbonate and plaster of Parisare also blended with Polyethylene and calcium carbide (Ferny *et al*., 2000; Mahmood *et al*., 2010). These materials provide bridging to water entry to calcium carbide through polyethylene frame work. Ferny *et al*. (2000) compared wax coated calcium carbide with polyethylene matrices regarding acetylene release and nitrification inhibition. Another comparison was made by Mahmood (2009) among seven encapsulations. He noted acetylene and ethylene flux from the surface of soil incubated with various CaC_2 encapsulations up to ninety one days. The data regarding soil ammonium and nitrate concentrations and acetylene and ethylene flux at 35th day of incubation is presented in Table 1. It is evident from the results that polyethylene blended calcium carbide released acetylene slowly. Maximum ammonium and minimum nitrate was noted in treatment with calcium carbide blended with 58% polyethylene. Nitrification inhibition was decreased with decreasing the polymer percentage in the polyethylene encapsulations. High concentrations of ethylene with encapsulations of low acetylene flux might be due to the provision of acetylene for microbial reduction for longer periods than in case with rapid release where there are more chances of its escape (Table 1).

Encapsulated calcium carbide (ECC) as nitrification inhibitor: Encapsulated calcium carbide as nitrification inhibitor was evaluated probably for the first time in 1988 (US Pat. Appl.07/229,386, 8 Aug. 1988). Banerjee and Moiser (1989) used wax coating as encapsulation. They found ECC an effective NI for flooded and dry conditions in uncultivated soil. They also noted that the inhibition was not stopped for longer periods of time but delayed and recovered shortly after vanishing of ECC in soil.

A number of researchers confirmed the effectiveness of ECC as NI in soils cultivated with various crop plants (Ferny *et al*., 1992; Keerthisinghe *et al*., 1995). In soil with alternative cultivation of wheat and rice, ECC enhanced ammonium and total nitrogen contents. The application of ECC also negatively affected the bacterial populations responsible for ammonia oxidation. Not only the nitrification but dehydrogenase and nitrate reductase activities were also reduced (Patra *et al*., 2006).

Table 1.Comparison of different calcium carbide encapsulations on soil acetylene and ethylene flux, and nitrate and ammonium concentrations at 35thday of incubation

Type of encapsulation	Acetylene Flux (ng m^{-1} min^{-1})	Ethylene flux (ng m^{-1} min^{-1})	Nitrate-N (mg kg^{-1})	Ammonium-N (mg kg^{-1})
Control	0.00 d	0.006 f	181.6 a	5.33 f
Filled in medical capsules	0.26 d	0.104 e	89.6 b	100.7 e
Coated with beeswax	5.50 c	0.110 e	50.3 c	130.3 d
Coated with paraffin wax	4.90 c	0.134 d	52.0 c	135.7 d
Coated with black enamel paint	7.94 b	0.172 c	46.3 cd	150.7 c
Blended with 58% polyethylene	9.68 a	0.213 a	38.0 d	163.7 a
Blended with 48% polyethylene	8.73 ab	0.192 b	42.0 cd	157.0 b
Blended with 34% polyethylene	0.14 d	0.110 e	91.6 b	102.7 e
LSD ($p \leq 0.05$)	1.02	0.013	10.14	5.42

22.5 g kg^{-1} calcium carbide was applied through either encapsulation. Soil in each pot was mixed with 1 g kg^{-1} ammonium sulfate (Mahmood, 2009).

In flooded water, 50% of the applied N was lost when urea was broadcasted. Total N loss from the applied nitrogen was significantly reduced when urea was either incorporated or deep placed in the presence of ECC (Keerthisinghe *et al*., 1996). In a wheat field, wax coated calcium carbide limited ammonium oxidation, prevented nitrogen loss by denitrification for 75 days and resultantly increased N accumulation by wheat plants. Thus, a 46% greater recovery of applied nitrogen was observed in the plant-soil system at harvest. However, the inhibitor treatment did not increase grain yield because of water logging at the end of tillering and during stem elongation (Ferny *et al*., 1992). Increase in nitrogen accumulation in wheat tops, owing to nitrogen transformations with ECC is also reported by Smith *et al*. (1993).

Soil application of ECC also affected gaseous emissions from soil surface. The emissions of N_2, N_2O and CH_4 were strongly mitigated with ECC (Bronson and Mosier, 1991). Under field conditions with corn as a test crop, Bronson *et al*. (1992) banded ECC (at 0, 20, or 40 kg ha^{-1}) with urea (218 kg N ha^{-1}) 7 weeks after planting. Between 1 and 14 weeks after fertilization, N_2O losses of 3226, 1017, and 1005 g N_2O-N ha^{-1} from urea alone, urea plus 20 kg ECC $ha^{-1}$and 40 kg ECC ha^{-1}, respectively, were measured from vented chambers. Nitrous oxide was positively correlated with soil NO_3 levels, indicating that nitrification inhibitor indirectly controlled N_2O emissions by preventing NO_3 from accumulating in the soil. However, carbon dioxide emissions from root zone were not affected by ECC in that study.

Use of ECC is not always beneficial in every case. In a flooded rice field ECC (wax coated) significantly inhibited nitrification, however, the practice increased the loss through ammonia volatilization in soil with pH of 8.0-8.5 (Chaiwanakupt *et al*., 1996).

C**omparison of ECC with other nitrification inhibitors:** Owing to variations in rate and method of application, it is a difficult task to equitably compare available NI,s under a single set of experimental conditions. However, researchers made comparisons by scarifying one or the other factor. For instance, with flooded rice as test crop, Aulakh *et al*. (2001) compared ECC, ATC (4-amino- 1,2, 4-triazole) and DCD. Up to 10 days of incubation ECC inhibited nitrification by 93%, however, the effect of ATC was more sustainable. At 20th day of incubation soil ammonium nitrogen concentrations were 96, 58 and 38% of applied ammonium-N in treatments with ECC, ATC and DCD, respectively.

In another experiment with dry seeded flooded rice, ECC (wax coated) and nitrapyrin were used individually for nitrification inhibition. Under those specific soil and environmental conditions ECC inhibited nitrification much better than nitrapyrin. Compared to control 84% nitrogen was recovered with ECC whereas in case of nitrapyrin recovery was only 43% (Keerthisinghe *et al*., 1993). In the same way in cotton field N losses were more effectively reduced with acetylene (57%) compared to that of 48% with nitrapyrin (Chen *et al*., 1994).In a vented chamber study, during the first year, nitrous oxide emissions were almost similar from the fields treated with ECC and nitrapyrin. However, in the second year 521 g N ha^{-1} was lost more from the field with ECC than that of nitrapyrin (Bronson *et al*., 1992).Combined effect of ECC or DCD with a urease inhibitor hydroquinone was studied by chen *et al*.

(1998). They noted a better urea-N recovery and grain yield with DCD combination than that of ECC with hydroquinone.

Encapsulated calcium carbide, an ethylene source: A part of acetylene released from ECC in soil may reduce to ethylene by soil indigenous microbes having nitrogenase enzyme activity (Yaseen *et al*., 2006; Kashif *et al*., 2007). Ethylene is a gaseous phytohormone, whether endogenously synthesized in the plant body (Lurssen, 1991) or supplied exogenously it has marked effects on plant growth and development (Arshad and Frankenberger, 2002). It stimulates the germination of seeds which may be inhibited due to embryo or coat dormancy, adverse environmental conditions or inhibitors (Beaudoin *et al*., 2002; Ghassemian *et al*., 2002). However, sometimes it delays or does not affect seed germination (Esashi *et al*., 1991).

Response of plant roots to exogenously applied ethylene varies with gas concentration as well as plant species. Short term exposure of roots to ethylene significantly increased root hydraulic conductivity, root oxygen uptake and stomatal conductance in hypoxic seedlings (Kamaluddin and Zwiazek, 2002).

Ethylene also hasincredible effects on shoot growth of plants. Robert *et al*. (1998) found a 22% decrease in plant height of Tifton 85" burmudagrass (*Cynodon dactylon* L.) by the application of ethephon (an ethylene releasing compound).They also noted node swelling, bud swelling at the crown, terminal leaf necrosis and chlorotic stripping of young developing leavesunder the influence of ethylene.Reduction in plant height due to ethylene is also reported by Rajala and Peltonen-Saino (2001) and Rajala *et al*. (2002).

Ethephonandmepiquat chloride, alone and in mixtures, stimulatedtillering and occasionally increased the number of spike-bearingtillers (Klassen and Bugbee, 2002).Ethephon typically increases barley *(Hordeum vulgare* L.) spikes per square meter by increasing the frequency of late emerging green tillers, resulting in uneven crop maturity (Lauer, 1991).

Soil applied encapsulated calcium carbide slowly react with water to produce acetylene which is reduced to ethylene by soil indigenous microbes (Yaseen *et al*., 2006; Kashif *et al*., 2007). Acetylene being a nitrification inhibitor gas and ethylene as a plant growth regulator are important in affecting soil nitrogen economy and crop plant growth and yield parameters (Mahmood *et al*., 2002).

Effect of ECC on growth and yield of crops: Calcium carbide application affects growth and yield of crops by changing the amount and form of available nitrogen through nitrification inhibition and by providing ethylene exogenously. Crop response to ECC varies with soil properties, crop type and extent and nature of nitrogen losses under a given set of soil and environmental conditions. Other factors include type of encapsulation, rate, time and depth of application of ECC. They encapsulated powdered CaC_2 in medical capsules and applied at 30, 60, 90 and 120 kg ha^{-1} with and without NPK fertilizers at three times i.e. at sowing, two and four weeks after sowing. Number of tillers, root dry weight, 1000-grain weight, grain yield, straw yield and N uptake increased significantly by the application of ECC plus NPK compared to that of NPK alone. Results indicated that application of ECC at 60 kg ha^{-1} applied two weeks after sowing seemed appropriate rate as maximum number of tillers, root weight, grain yield and N uptake were obtained by this treatment. They found that, compared to control, ECC applied at two weeks after sowing of wheat significantly improved nitrogen economy and yield of the crop (Fig. 1). It can be perceived from the results that two weeks after sowing might be the best time to inhibit nitrification for better uptake of nitrogen by wheat.

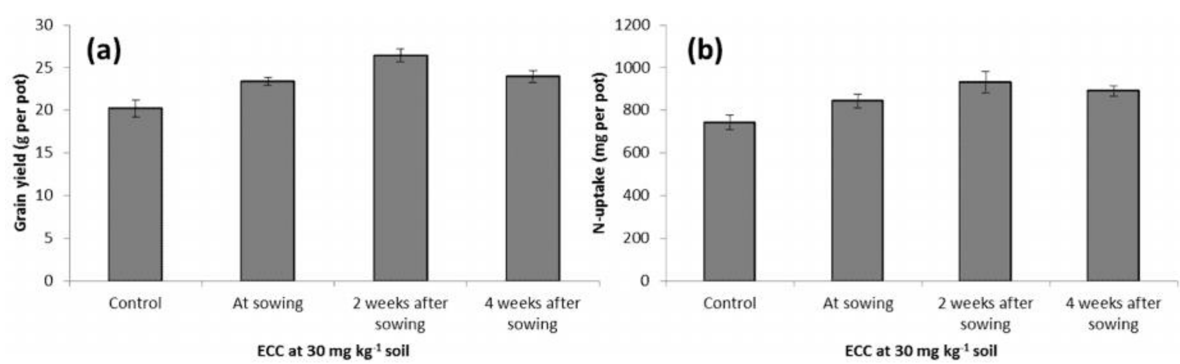

Figure 1. Effect of time of application of encapsulated calcium carbide (ECC) on grain yield (a) and nitrogen uptake of wheat (Mahmood *et al*., 2005).

Application depth of ECC in the soil can also influence the effectiveness of ECC as nitrification inhibitor. It is because of the reason that volume of soil above the ECC particles directly controls the entrapment of acetylene released from ECC. Entrapped acetylene accordingly affectsnitrification inhibition, nitrogen economy and ultimatelyyields parameters of a crop. We studied the impact of application depth of ECC (polyethylene blended) on various parameters of wheat (Mahmood *et al*., 2011). Grain yield and nitrogen uptake of wheat was significantly higher in the treatments where ECC was applied at 8 cm soil depth compared to that where application was done on the soil surface, or at 4 or 12 cm soil depth (Fig. 2).

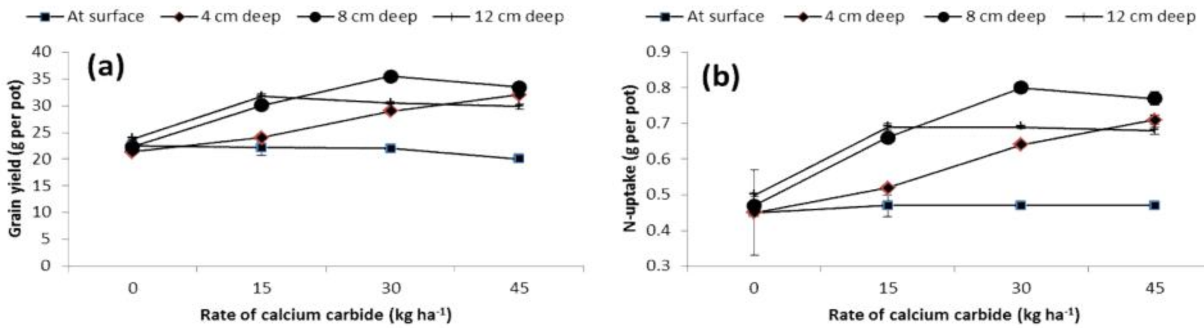

Figure 2. Effect of application depth of encapsulated calcium carbide (ECC) on grain yield (a) and nitrogen uptake of wheat (Mahmood *et al*., 2011).

In both the experiments similar response of nitrogen uptake and wheat grain yield to ECC application was noted.This indicates that nitrogen concerns of ECC application are more prominent in these studies than ethylene release. Increase in economical yield of wheat owing to better N uptake with ECC application has also been reported by Ahmad *et al*. (2004) and Yaseen *et al*. (2004).

Scattered information is available regarding the best type and effective rate of ECC for various crops. For instance, Saleem *et al*. (2002) conducted a field experiment to evaluate the influence ECC on growth, yield and chemical composition of okra. They found CaC_2 application at 90 kg $ha^{-1}$the most effective in increasing horizontal expansion of plant, yield of green pods, number of green pods per plant, fresh and dry weights of shoot and root. The plant height was decreased with an increase in ECC application rate. Due to the synergistic effect of N uptake, phosphorus and potassium contents in green pods and roots were also improved ECC application.

Positive response of okra to ECC application was also reported by Kashif *et al*. (2007) and (2008). They applied ECC6 cm deep in soil at 30 and 60 kg $ha^{-1}$and two weeks after germination.Okra showed an increase in green pod yield up to 37% in treatment where ECC was applied at 60 kg ha^{-1} along with half of the recommended N fertilizer (60 kg N ha^{-1}), whereas, the increase was about 19% compared to that of with recommended nitrogen fertilizer (120 kg N ha^{-1}) alone.

Encapsulated calcium carbide plus recommended NPK fertilizers application increased the paddy yield by 19 % compared to recommended NPK fertilizers alone (Rahim *et al.*, 2004). Beneficial effects of ECC application on rice growth and yield has also been reported by Yaseen *et al*. (2005). They noted that ECC applied alone or along with chemical fertilizer to flooded rice, significantly increased early emergence of panicles, number of tillers and paddy yield.

In a field experiment, calcium carbide coated urea reduced N losses and increased fertilizer N recovery and rice yield (Hazzrika and Sarkar, 1996). However, in case where soil nitrogen losses via leaching and denitrification were not significant, application of ECC delayed the disappearance of ammonia derived from urea but did not improve yield of maize (Randall *et al*., 2001).

Conclusion: Encapsulated calcium carbide is a good nitrification inhibitor in soils. It reduces losses of nitrogen through nitrate leaching and denitrification, which in turn results in better nitrogen use efficiency and crop yields. Benefits related to ECC application are strongly influenced by a number of factors particularly the amount and nature of hydrophobic material used in encapsulation, rate, time and depth of application, soil and crop type, and severity of nitrogen losses in a particular set of soil and environmental conditions. Until now, amongst the materials used for encapsulation of CaC_2, polyethylene is the best in slowing down acetylene release from ECC. However, sometoxic effects of polyethylene are reported on plant growth.

Among the limitations in ECC application are the high cost of encapsulation and the moisture entrapment at the time of encapsulation; which reduces its efficiency during storage. More sophisticated, mechanized protocol and large scale production are required to ensure minimum cost and moisture free encapsulation. It is also need to research some newhydrophobic materials in encapsulation which do not stay in soil toolong to pollute it; instead decompose along with the calcium carbide particles.

A big gap in ECC research is the confusion that whether a particular effect on plant growth is due to nitrification inhibition or ethylene; which is produced by the reduction of ECC released acetylene. For instance, the better nitrogen uptake of plants, the credit of which is mostly given to nitrification inhibition, may be due to better root growth under the influence of ethylene. The scenario becomes more complicatedby the fact that nitrogen uptake by plant and its root growth are positively correlated. For the case where soil nitrification inhibition with ECC did not improve crop N economy, logic is given by considering the N losses from the system negligible. The other option related to restricted root growth with high ethylene concentrations is neglected. Questions are also unanswered about entry of acetylene in the plant body and its direct influence on growth of different plant species.

These research gaps may be filled by careful determination of acetylene and ethylene released from ECC and by including the treatments of pure acetylene and ethylene application in experimental plans.

Effects of soil physical and chemical properties on a calcium carbide encapsulation, acetylene release and acetylene stay in soil are not studied well. For the successful diffusion of the approach among farming community, it is necessary to identify the soils and climatic conditions where ECC application would always give benefits to agriculture. Moreover, the approach efficacy may be further improved by blending ECC with fertilizers which would ensure acetylene release closer to the fertilizer nitrogen.

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