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Review/synthesis

Natural nitrification inhibitors for higher nitrogen use efficiency, crop yield, and for curtailing global warming

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Abstract

Nitrification inhibitors selectively inhibit microbial enzymes responsible for the conversion of NH_4^+ to NO_3^-. Arresting nitrification could be a key strategy to improve nitrogen (N) recovery and agronomic N use efficiency in situations where the loss of N is significant. Although chemicals known to inhibit nitrifiers have been tested, many of these are still at the experimental level; high cost, limited availability, adverse influence on beneficial soil microorganisms, and above all, poor extension and promotional activities are major constraints in this respect. It is therefore necessary to develop plant-based nitrification inhibitors (natural nitrification inhibitors, NNI) for augmenting nitrogen use efficiency, crop productivity, and for safeguarding the environment. The advantages of NNI are that they are easily available, cheap, and eco-friendly. This paper briefly reviews the different aspects of plant-based nitrification retarders.

Keywords: Eco-friendliness, Crop yield, Nitrifiers, Plant-derived nitrification retarders.

Introduction

Nitrification, a microbial process, is a key component and integral part of the soil nitrogen (N) cycle. It is the biological oxidation of ammonia (NH_3) to nitrate (NO_3^-) and is carried out by two groups of chemolitho-trophic bacteria (*Nitrosomonas* spp. and *Nitrobacter* spp.), which are ubiquitous on earth (Norton et al., 2002). In agricultural systems, rapid and unchecked nitrification, however, results in inefficient N use, N leakage, and environmental pollution (Subbarao et al., 2009). The NO_3^- formed, is highly susceptible to losses from the root zone by leaching and/or denitrification (Subbarao et al., 2006). Loss of N from the root zone has large economic implications, to the tune of 15 billion US$ annually, just as fertilizer losses alone, besides the unknown cost of environmental consequences such as nitrate (NO_3^-) pollution of ground water, eutrophication of surface waters, and atmosphere pollution.

Management of nitrification by the application of chemical inhibitors is a proven strategy to improve N recovery, agronomic N use efficiency (NUE), and for limiting environmental pollution (Sahrawat and Keeney, 1985; Subbarao et al., 2006; Prasad, 2009). Several synthetic chemicals capable of inhibition of urea hydrolysis or nitrification in soils have been evaluated. Examples include N-serve (nitrapyrin), dicyandiamide (DCD), AM (2-amino-4 chloro-6 methyle pyrimidine), sodium chlorate, sodium azide, and benzene hexachloride ($C_6H_6Cl_6$). Many of these products, however, have been restricted to the experimental stage because of the high

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cost, limited availability, and adverse influence on beneficial soil microorganisms and, above all, poor extension and promotional activities for taking the technology to the farmers. Plant based nitrification inhibitors, which are eco-friendly and biodegradable, therefore hold considerable promise. Indeed, suppression of soil nitrification has been observed in some natural ecosystems (natural nitrification inhibition). It aims conservation of soil N and improved N status through development of low NO_3^- ecosystems (Lata et al., 2004; Subbarao et al., 2006).

Several empirical studies have indicated that some plants and their byproducts inhibit nitrification (Prasad et al. 1971; Lata et al., 2004; Patra et al., 2006; 2009; Kiran and Patra, 2002; Kiran et al., 2003). *Brachiaria humidicola* (Rendle) Schweick, karanj (*Pongamia glabra* Vent.), sweet sorghum (*Sorghum bicolor* (L.) Moench), neem (*Azadirachta indica* Adr. Juss.), tea (*Camellia sinensis* (L) O'kuntze), linseed oil (*Linum usitatissimum* L.), mahuwa (*Madhuca latifolia* (Roxb.) J.F. Macbr.), *Pyrethrum* spp., *Artemisia annua* L. and mint (*Mentha spicata* L.) are important sources of natural nitrification inhibitors (NNI). However, the concept remained largely unsupported for lack of an appropriate methodology to conclusively demonstrate *in situ* inhibition of nitrification by such plant derived chemicals (Subbarao et al., 2006). The reason may be lack of commercial product development using such chemical compounds. The objective is to review the recent literature on NNI and highlight its potential to promote N use efficiency and prevent environmental contamination.

Nitrification inhibition: the way forward

Nitrogenous fertilizers are predominantly of the form of NH_4^+ or urea, which on application is rapidly converted to nitrate by the nitrifying bacteria. Being a negatively charged ion, NO_3^- does not bind strongly to the soil, and is liable to be leached out of the root-zone, while NH_4^+ is strongly held by electrostatic forces to the negatively charged clay surfaces and soil organic matter. Nitrification inhibitors, including commercial products like N-Serve or nitrapyrin, dicyandiamide (Amberger, 1989) and DMPP (3,4-dimethylpyrazolephosphate) (Zerulla et al., 2001) inhibit the ammonia monoxygenase enzyme and prevent the transformation of NH_4^+ to NO_3^-, implying specificity in their mode of action (Prasad, 2009). Microbial degradation of nitrification inhibitors, however, occurs in the soil over a range of temperatures (10–158°C: Puttanna et al., 1999; Di and Cameron, 2004). This together with the leaching of inhibitors, especially DCD from the active zone of nitrification often leads to inconsistent performance under field conditions. The high cost of synthetic inhibitors is yet another factor that precludes its large-scale use in agriculture where profit margins are relatively small and the return from investment is uncertain. Synthetic nitrification inhibitors also have limited availability and have detrimental effects on the environment, further highlighting the need to develop NNI, as a sound alternate strategy.

Natural Nitrification Inhibitors

It is well known that certain plant species are sources of organic molecules/compounds that specifically inhibit nitrification (Table 1). Vyas et al. (1981) developed Nimin® (tetranortriterpenoids) by extracting the neem cake with ethanol and reported an enhancement of apparent N recovery by 25–30% as compared to the uncoated urea. A schematic presentation of the NNI concept along with their benefits is presented in Fig. 1. As mentioned, suppression/inhibition of nitrification will minimize various processes leading to N leakage (i.e., NO_3^- leaching and gaseous nitrous oxide emissions), and facilitate N flow through NH_4^+. The assimilation of NH_4^+ also requires much less metabolic energy than NO_3^-, leading to a higher NUE in agricultural systems.

In experimental studies, Patra et al. (2002) found that NNIs significantly increased herb and essential oil yield of mint compared to prilled urea without coating and were as effective as DCD. Inhibition of nitrification and increase in fertilizer N use efficiency by nimin and *M. spicata* oil suggest that these materials can be used for retardation of nitrification in soils. Patra et al. (2006) further reported that urea hydrolysis was inhibited by these natural products along with nitrification and the intensity of inhibition was dependent on the level of coating materials used. With 0.5% coating, urea

Table 1. Natural nitrification inhibition (NNI) properties in different plants.

Plant species	Chemical/ plant part involved	NNI effect	References
Neem (*Azadirachta indica* Adr. Juss.)	Neem seed extractand neem oil emulsion	Increased N use efficiency, test weight, and grain yield of rice	Bains et al. (1971); Reddy and Prasad (1975); Prasad et al. (1999; 2002).
Koronivia grass (*Brachiaria humidicola* (Rendle) Schweick)	Root exudates	Nitrification inhibited for ~50 days	Ipinmorti et al. (2008); Subbarao et al. (2007)
Karanj (*Pongamia glabra* Vent.)	Karanjin (seed extract)	Highly efficient nitrification inhibitor (62–75%) and a N_2O mitigator (92–96% reduction in N_2O emission), potential nitrification inhibitor and mitigator of N_2O emission	Majumdar (2002); Sahrawat and Mukherjee (1997)
Mint (*Mentha spicata* L.)	Dementholated oil (1%) coated urea	Significantly retarded urease activity, as well as *Nitrosomonas* and *Nitrobacter* activities	Patra et al. (2006)
Karanj (*P. glabra*)	Karanj cake	NNI properties	Prasad et al. (1971)
Mint (*M. spicata*)	Essential oil	Increased N use efficiency up to 30–35%	Patra et al. (2001; 2002)

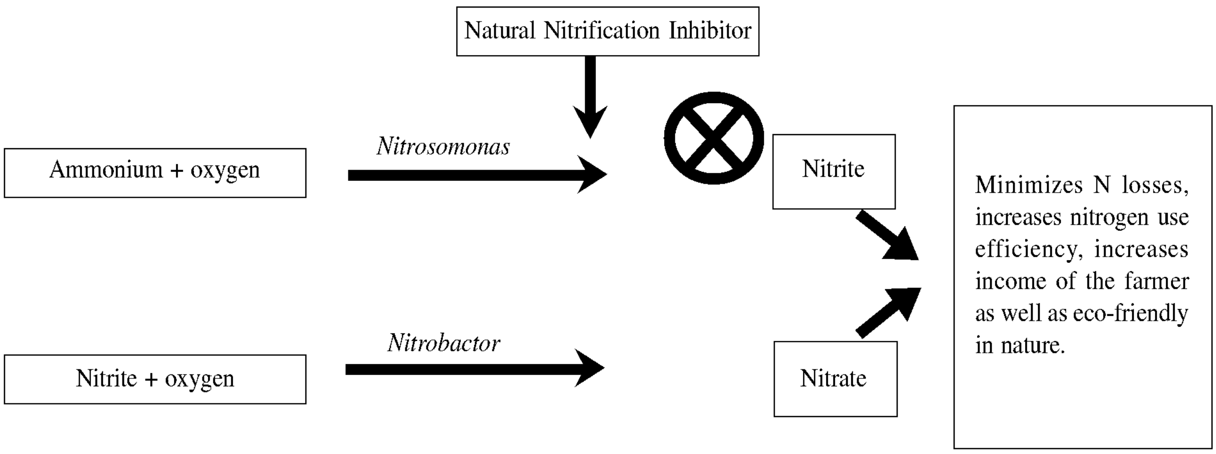

Figure 1. Schematic presentation of the natural nitrification inhibitors.

hydrolysis was inhibited in the decreasing order of DMO (dementholated oil)> terpenes> DCD> *M. spicata* oil; whereas at 1% coating, inhibition followed the order: terpenes> DMO> *M. spicata* oil> DCD. At 0.5% coating nitrification inhibition decreased in the order: *M. spicata* oil> DCD> DMO> terpenes; while at 1% coating, the order was DCD> DMO> *M. spicata* oil> terpenes. All these natural products (DMO, terpenes, and *M. spicata* oil) significantly retarded soil urease activity besides *Nitrosomonas*, *Nitrobacter*, and total bacterial, and actinomycete populations. These coating materials, unlike DCD, could be retardants of urease activity as well, besides nitrification, while DCD is a retardant of nitrification with little or no effect on urea hydrolysis. The natural products (NNI), unlike chemical nitrification inhibitors, are also less persistent, bio-degradable, eco-friendly, and cheap.

Advantages of natural nitrification inhibitors

As can be seen from Table 2, most NNIs increased N recovery of crops by 25 to 30% compared to uncoated urea. Natural nitrification inhibitors also extend the time of N availability for plant uptake (Shaviv and Mikkelsen, 1993). In general, NNI blended fertilizers are produced by encapsulating or giving a protective coating (water-insoluble, semi-permeable, or impermeable with pores) to the conventional soluble fertilizer materials. Encapsulation controls water entry and rate of dissolution, making nutrient release and availability more synchronized with plant requirement (Fujita et al., 1992). It also improves soil health by reducing N losses and would also enhance crop productivity.

In India, experiments have been conducted on major crops viz., rice (*Oryza sativa* L.), corn (*Zea mays* L.), wheat (*Triticum aestivum* L.), potato (*Solanum tuberosum* L.), cotton (*Gossypium hirsutum* L.), and Japanese mint (*Mentha arvensis* L.f.) to evaluate the impact of NNIs on crop yield. In early seventies, some work on influence of neem cake and karanj cake coated urea on N use efficiency and crop yield was initiated at the Indian Agricultural Research Institute, New Delhi, India (Bains et al., 1971; Sahrawat, 1982). The experimental findings indicated a significant improvement in yields of rice and wheat with application of natural product coated urea. Similar results have been reported subsequently by many researchers from elsewhere in this country (Mishra et al., 1991; Patra et al., 2006; Prasad, 2009).

Reduced emission of N_2O, a potent greenhouse gas, is yet another advantage of NNI (Sahrawat and Keeney, 1986). Houghton et al. (1996) estimated that on a global scale 10–17 Tg (million tonnes) N_2O escapes from the N fertilized soils every year. Just as the chemically synthesized nitrification inhibitors, plant products, such as nimin and neem coated urea also may reduce gaseous N_2O emissions from rice production systems (Majumdar et al., 2000) and thus may offset global warming.

Natural nitrification inhibitors are also cheaper than the synthetic nitrification inhibitors because it is sourced from various types of grasses, agricultural crops, essential oil crops, plants or by their byproducts. Recent work on medicinal and aromatic plants and their oils/derivatives indicated strong ability to reduce nitrification (Patra et al., 2006; 2009). As the products (NNI) are obtained from naturally growing plants, they are eco-friendly, and are also easily available in the rural areas or can be included in the farming systems, implying lower cost of production compared to synthetic nitrification inhibitors. There are, however, certain constraints which make NNI less acceptable. Lack of research and product development (RPD), poor extension and inefficient promotional activities, absence of regulatory control on its use in agriculture, and difficulties in the extraction and purification of the compounds are important in this context; most of these, however, can be overcome by organized research, extension, and marketing efforts.

On a final note, NNIs can be exploited to develop a range of biological and chemical strategies for controlling nitrification in agricultural systems. Moving away from

Table 2. Plant product/ byproduct, derivatives used as nitrification inhibitors (NI) and the relative efficiency for promotin N use efficiency.

Nitrification inhibitors	Source	Increase in NUE (%) compared to no NI	References
Neem cake/Neem oil emulsion	*Azadirachta indica* Adr. Juss.	20–25	Bains et al. (1971); Prasad et al. (1999)
Nimin	*A. indica* oil	25–30	Vyas et al. (1981)
Citrullus cake	*Citrullus colocynthis* (L.) Schrad.	20–25	Jain et al. (1980)
Karanj cake	*Pongamia glabra* Vent.	20–25	Prasad et al. (1971)
Karanjin	*P. glabra* seeds	20–25	Sahrawat (1981a; b)
Mint essential oil	*Mentha spicata* L.	30–35	Patra et al. (2001; 2002; 2009)
Byproducts	Medicinal and aromatic plants	30–35	Kiran and Patra (2003)
Byproducts	Natural essential oils	20–25	Kiran et al. (2003)

NO_3^- dominated production systems will help develop environmentally responsible and sustainable production systems where NNIs have an important role. Such production systems would also reduce the undesirable impact of N fertilizers on the global environment. Overall, NNIs are economically effective and eco-friendly materials which need be promoted among the farming community. Up-scaling the extension activity holds the key in this regard.

References

Amberger, A. 1989. Research on dicyandiamide as a nitrification inhibitor and future outlook. Commun. Soil Sci. Plant Anal., 20: 1933–1955.

Bains, S.S., Prasad, R., and Bhatia, P.C. 1971. Use of indigenous plant materials to enhance N use efficiency of fertilizer nitrogen for rice. Fert. News, 16: 30–32.

Di, H.J. and Cameron, K.C. 2002. The use of a nitrification inhibitor, dicyandiamide (DCD) to decrease nitrate leaching and nitrous oxide emissions in a simulated grazed and irrigated grassland. Soil Use Manage. 18: 395–403.

Fujita, T., Yamashita, Y., Yoshida, S., and Yamahira, K. 1992. Granular fertilizer with a decomposable coating and process for producing the same. Canadian Patent No. CA 1, 295, 849, pp 57. Issued Feb. 18, 1992. Applied in Japan on Aug. 5, 1986. Assigned to Chisso Corp., Japan.

Houghton, J.T., Meira Filho, L.G., Callander, B.A., Harris, N., Kattenberg, A., and Maskell, K. 1996. Climate Change 1995 The science of climate change. Cambridge University Press, Cambridge, 572p.

Ipinmorti, R.R., Watanabe, T., and Ito, O. 2008. Effect of *Brachiaria humidicola* root exudates, rhizosphere soils, moisture and temperature regimes on nitrification inhibition in two volcanic ash soils of Japan. World J. Agric. Sci., 4(1): 106–113.

Jain, J.M., Narayanasamy, G., Sarkar, M.C., and Datta, M.N. 1980. An evaluation of nitrification retardation property of *Citrullus colosynthis* cake and its influence on yield and N uptake by wheat. J. Indian Soc. Soil Sci., 28: 480–484.

Kiran, U. and Patra, D.D. 2002. Augmenting yield and Urea-N utilization efficiency in wheat (*Triticum aesitivum*) through use of natural essential oils and dicyandiamide coated urea in light textured soils of central Uttar Pradesh, India. Commun. Soil Sci. Plant Anal., 33: 1375–1388.

Kiran, U. and Patra, D.D. 2003. Medicinal and aromatic plant materials as nitrification inhibitors for augmenting yield and nitrogen uptake by Japanese mint (*Mentha arvensis*). Bioresour. Technol., 86: 267–276.

Kiran, U., Patra, D.D., and Kumar, S. 2003. Influence of natural essential oils and their byproducts as nitrification retarders in regulating nitrogen utilization for Japanese mint in sandy loam soils of subtropical Central India. Agric. Ecosyst. Environ., 94: 237–245.

Lata, J.C., Degrange, V., Raynaud, X., Maron, P.A., Lensi, R., and Abbadie, L. 2004. Grass populations control nitrification in savanna soils. Funct. Ecol., 18: 605–611.

Majumdar, D. 2002. Suppression of nitrification and N_2O emission by karanjin- a nitrification inhibitors prepared from karanjin (*Pongamia glabra* Vent.). Chemosphere, 47: 845–850.

Majumdar, D., Kumar, S., Pathak, H., Jain, M.C., and Kumar, U. 2000. Reducing nitrous oxide emission from and irrigated rice field or north India with nitrification inhibitors. Agric. Ecosyst. Environm., 81: 163–169.

Mishra, S.S., Singh, S.J., Gogoi, A.K., and Sinha, K.K. 1991. Nitrogen use efficiency by nitrogen and weed management in rice-wheat sequence. Indian J. Agron., 36: 306–312.

Norton, J.M., Alzerreca, J.J., Suwa, Y., and Klotz, M.G. 2002. Diversity of ammonia monooxygenase operon in autotrophic ammonia oxidizing bacteria. Arch. Microbiol., 177: 139–149.

Patra, D.D., Anwar, M., Chand, S., Kiran, U., Rajput, O.K., and Kumar, S. 2002. Nimin and Mentha spicata oil as nitrification inhibitors for optimum yield of Japanese mint (*Mentha arvensis*). Commun. Plant Soil Anal., 33 (3&4): 451–460.

Patra, D.D., Anwar, M., Chattopadhyay, A., Prasad, A., Pande, P., Kumar, A., Singh, S., Srivastava, R.K., Krishna, A., Singh, V., Tomar, V.K.S., Bansal, R.P., Singh, A.K., Singh, K., Bahl, J.R., and Kumar, S. 2001. Use of mint essential oil as an agrichemical: control of N-loss in crop fields by using mint essential oil coated urea as fertilizer. Curr. Sci., 81(12): 1526–1528.

Patra, D.D., Kiran, U., Chand, S., and Anwar, M. 2009. Use of urea coated with natural products to inhibit urea hydrolysis and nitrification in soil. Biol. Fertil. Soils, 45: 617–621.

Patra, D.D., Kiran, Usha, and Pande, Preeti. 2006. Urease and nitrification retardation properties in natural essential oils and their by- products. Commun. Soil Sci. Plant Anal., 37: 1663–1673.

Prasad, R. 2009. Efficient fertilizer use: The key to food security and better environment. J. Trop. Agric., 47 (1-2): 1–17.

Prasad, R., Rajale, G.B., and Lakhdive, B.A. 1971. Nitrification retarders and slow release nitrogenous fertilizers. Adv. Agron., 23: 337–405.

Prasad, R., Sharma, S.N., Singh, S., Devakumar, C., Saxena, V.S., and Shivay, Y.S. 2002. Neem coating of urea for the environment and agriculture. Fert. News, 47(5): 63–67.

Prasad, R., Singh, S., Saxena, V.S., and Devkumar, C. 1999. Coating of prilled urea with Neem (*Azadirachta indica* Juss.) oil for efficient nitrogen use in rice. Naturwissenschaften, 86: 538–539.

Puttanna, K., Gowda, N.M.N., and Rao, E.V.S.P. 1999. Effect of concentration, temperature, moisture, liming and organic matter on the efficacy of the nitrification inhibitors benzotriazole, o-nitrophenol, m-nitroaniline and dicyandiamide. Nutr. Cycl. Agroecosys., 54: 251–257.

Reddy, R.N.S., and Prasad, R. 1975. Studies on the mineralization of urea, coated urea and nitrification inhibitor treated urea in soil. J. Soil Sci., 26: 304–312.

Sahrawat, K.L. 1981a. Karanj (*Pongamia glabra* Vent.) as source of nitrification inhibitor. Fert. News, 26: 29–33.

Sahrawat, K.L. 1981b. Comparison of karanjin with other nitrification inhibitors for retardation of nitrification of urea in soil. Plant Soil. 59: 494–498.

Sahrawat, K.L. 1982. Comparative evaluation of karanjin and extract of Karanj (*Pongamia glabra* Vent) and neem (*Azadirachta indica*) seeds for retardation of nitrification of urea in soil. J. Indian Soc. Soil Sci., 30: 156–159.

Sahrawat, K.L. and Keeney, D.R. 1985. Perspectives for research on development of nitrification inhibitors. Commun. Soil Sci. Plant Anal., 16: 517–524

Sahrawat, K.L. and Keeney, D.R. 1986. Nitrous oxide emission from soils. Adv. Soil Sci., 4: 103–148.

Sahrawat, K.L. and Mukherjee, S.K. 1997. Nitrification inhibitors. I Studies with karanjin, a furanol flavonoid from karanja (*Pongamia glabra*) seeds. Plant Soil. 47: 27–36.

Shaviv, A. and Mikkelsen, R.L. 1993. Controlled-release fertilizers to increase efficiency of nutrient use and minimize environmental degradation – A review. Fert. Res., 35: 1–12.

Subbarao, G.V., Ito, O., Sahrawat, K.L., Berry, W.L., Nakahara, K., Ishikawa, T., Watanabe, T., Suenaga, K., Rondon, M., and Rao, I.M. 2006. Scope and strategies for regulation of nitrification in agricultural systems – Challenges and opportunities. Crit. Rev. Plant Sci., 25: 1–33.

Subbarao, G.V., Nakahara, K., Hurtado, M.P., Ono, H., Moreta, D.E., Salcedo, A.F., Yoshihashi, A.T., Ishikawa, T., Ishitani, M., Ohnishi-Kameyama, M., Yoshida, M., Rondon, M., Rao, I.M., Lascano, C.E., Berry, W.L., and Ito, O. 2009. Evidence for biological nitrification inhibition in *Brachiaria* pastures. Proc. Nat. Acad. Sci. USA, 106: 17302–17307.

Subbarao, G.V., Wang, H.Y., Ito, O., Nakahara, K., and Berry, W.L. 2007. NH_4^+ triggers the synthesis and release of biological nitrification inhibition compounds in *Brachiaria humidicola* roots. Plant Soil, 290: 245–257.

Vyas, B.N., Godrej, N.B., and Mistry, K.B. 1981. Development and evaluation of neem extract as a coating of urea fertilizer. Fert. News, 2: 19–25.

Zerulla, W., Barth, T., Dressel, J., Erhardt, K., Von Locquenghien, K.H., Pasda, G., Radle, M., and Wissemeier, H. 2001. 3,4-Dimethylpyrazole phosphate (DMPP) - a new nitrification inhibitor for agriculture and horticulture. Biol. Fert. Soils, 34: 79–84.