Nitrification inhibitors in agriculture and horticulture: A literature review

JHG SLANGEN[1] and P KERKHOFF[2]

Preface. This literature survey is the English version of P. Kerkhoff and J.H.G. Slangen "Nitrificatieremstoffen in Land- en Tuinbouw, Interne Mededeling 54, Vakgroep Bodemkunde en Bemestingsleer, Landbouwhogeschool, Wageningen, 99 p, 1980", supplemented by reference to the literature of 1980 and a partly of 1981. The literature cited has been taken from sources in East and West Europe and North America.

Only crops common in the regions mentioned are involved. For this reason rice has not been included in the cereals. Aspects of controlling the nitrogen status in soils by, for instance, "controlled release fertilizers" are not discussed and no details of the effects of pesticides on the NO_3- and or NH_4- contents in soils are given here.

Abstract. This review of literature is focussed on the readily available nitrification inhibitors N Serve (2-chloro-6-(trichloromethylpyridine), DCD (dicyandiamide) and AM (2-amino-4-chloro-6-methylpyrimidine). Compounds such as Terrazole (5-ethoxy-3-trichloromethyl-1,2,4-thiadiazole), DCS (N-2,5-dichloro-phenyl-succinamic acid) and non synthetic inhibitors like "Neem" and "Karanjin" are only briefly discussed.

Some chemical characteristics of these inhibitors are summarized. The effects of such soil characteristics as texture, organic matter content, pH moisture content, O_2-pressure and temperature on their efficiency are being discussed. These aspects are seen in relation to yield and to the chemical composition of a number of agricultural (wheat, maize, grassland, oats) and horticultural (lettuce, spinach, tomatoes) crops.

Phytotoxicity, residual effects and residues in soils and plants of the most interesting compounds are reviewed as well as aspects of some effects of inhibitors on plant diseases.

Most of the compounds are more or less effective in keeping nitrogen in the NH_4-form thus leading to a relatively high content of NH_4-N over a shorter or longer period. In a number of situations this leads to more effective use of nitrogen, but not necessarily to higher yields. This increase of nitrogen efficiency can be explained by a decrease in leaching and or denitrification of nitrogen. Lower NO_3-contents in vegetables, found in some of the experiments with nitrification inhibitors, cannot be used to declare the products as generally useful in this respect. The uptake and assimilation of nitrogen by plants in their overall diversity cannot be regulated by adding a simple compound to the soil, not even in small quantities.

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[1] Department of Soil Science and Plant Nutrition, Agricultural University, De Dreijen 3, 6703 BC Wageningen, The Netherlands.
[2] Present address: Agricutlure Research Station POB 160, Paramaribo, Surinam.

This control can be achieved by the use of slow release fertilizers, by delaying ammonification or by inhibiting nitrifying organisms with more or less specific chemicals called inhibitors [72].

The use of inhibitors of nitrification may have positive aspects :

1. It minimizes the losses of nitrogen accompanying nitrification *Viz.* leaching and denitrification under situations where these losses are high [218] thus minimizing NO_3-pollution of ground and surface waters [85,169].
2. It keeps NO_3-contents in vegetables and forage crops at low levels so that one of the conditions for accumulation of NO_3 [48] is excluded or minimized [23,94,102,133].
3. From a practical point of view delay of nitrification might by useful in increasing N-efficiency if for one or another reason nitrogen has to be applied in autumn [11], or NH_4-nitrogen is given in one relatively high dose [166,167].

Keeping part of the whole amount of nitrogen in a growth medium in the NH_4-form has its consequences for uptake and assimilation of nitrogen by plants. Both NO_3^- and NH_4^+ can be taken up and metabolized by plants.

Nitrate is often an preferential source for crop growth as will be seen for instance for potatoes (5.3) and spinach (6.1) but much depends on plant species and environmental conditions [81]. NH_4-N uptake is best in an neutral medium and it is depressed as the pH decreases [137,190].

Ammonium-N can be toxic to plant growth. The mechanism of this toxicity is not yet understood, but the injury is more likely to occur at higher pH levels with relatively high NH_4 concentrations in soils [279].

Toxicity results in stunted and irregular growth of leaves, stems and midribs with, according to Polizotto et al. [183], decreasing starch synthesis, accumulation of amino acids and amides and a decreasing uptake of water and root exudation. Nitrate reductase activity (NRA) decreases with high amounts of NH_4-N as was found by Notton et al. [171] for turnips, cauliflower and radish by applying nitrapyrin (N-Serve) as a nitrification inhibitor.

As contrasted with these results of toxicity small additions of NH_4-N can be stimulating for growth as was found by Drouineau and Blanc [55], Cox and Reisenauer [49].

Detailed information about NH_4- and NO_3-nutrition of crops is given by Dijkshoorn [53] for ryegrass, Dijkshoorn and Ismunadji [54] for rice, Breteler and Smit [30] for wheat, and Kurvits and Kirby [104] for sunflower among others.

1. Introduction

The processes of the natural nitrogen cycle involved in the scope of this literature survey are:

1. proteolysis and ammonification
2. nitrification.

According to Mengel [133] proteolysis is the release of amino N from organic matter, the further reduction to NH_3 being called ammonification.

$$RHN_2 + H_2O \rightarrow NH_3 + ROH + \text{energy}$$

The bulk of the soil microflora is capable of bringing about the reactions mentioned; the heterotrophic organisms require organic C as an energy source. Factors that can retard the mineralization of organic soil N are those that depress the activity of the microorganisms, such as low temperature and a deficiency or an excess of water.

The biological oxidation of ammonia to nitrate is known as nitrification. Ammonia is first oxidized to NO_2 and this conversion is largely brought about by *Nitrosomonas*. NO_2 in turn is oxidized to NO_3 and this is effected by *Nitrobacter* species. These specialized groups of bacteria are obligately aerobic, so that they can only live in media where O_2 is available, and autotrophic. They prefer more neutral to slightly acid pH conditions [158]. In soils of low pH or in waterlogged soils the nitrification is thus restricted or even completely inhibited, resulting in accumulation of NH_4-N. Under favourable conditions for nitrifying bacteria ammonia is rather rapidly converted to NO_3 with no accummulation of NO_2 because the NO_2 formed is readily oxidized by *Nitrobacter* [87].

The two step oxidation from NH_4^+ to NO_3 takes place as follows:

$$\begin{array}{l} 2NH_4^+ + 3O_2 \rightarrow 2HNO_2 + 2H_2O + 2H^+ \\ 2HNO_2 + O_2 \rightarrow 2H^+ + 2NO_3 \\ \hline 2NH_4^+ + 4O_2 \rightarrow 2NO_3^- + 4H^+ + 2H_2O \end{array}$$

The net equation shows that nitrification is coupled with the release of H^+ and thus results in acidification of the medium.

Nitrifying bacteria oxidixe NH_4^+, either released by ammonification or applied as fertilizer.

Possible disadvantages of nitrification are losses of nitrogen by denitrification, leaching and or runoff, including movement of nitrate out of the crop root zone with, eventually, NO_3^- accumulation in ground and surface waters. As a result one may notice that a crop makes inefficient use of nitrogen. Prasad et al. [186] found N-efficiency for different crops to vary from 0.21 to 0.79; Nelson et al. [167] from 0.40–0.70. In the humid tropics Sahrawat and Mukerjee [276] found relatively low values of 0.25–0.40. This low efficiency often occurs also with horticultural crops.

Control of nitrification could lead to increased efficiency of nitrogen use with corresponding improvement in crop growth, yield and quality.

2 NITRIFICATION INHIBITORS ; GENERAL ASPECTS

2.1 Summary of nitrification inhibitors.

The discovery and use of Nitrapyrin (N-Serve, Dow Chemical Company) as an effective inhibitor of nitrification in soils [63,64,65] has greatly stimulated the interest in nitrification inhibitors. Numerous compounds have been proposed for regulating nitrification in soils, including organic and inorganic compounds, pesticides, chelating agents and plant products. A number of these as well as of urease inhibitors are manufactured and patented in the USA and Japan [189].

Prasad et al. [186] groups herbicides, insecticides, fungicides and fumigants as potential inhibitors. However, most of the herbicides and insecticides have no inhibitory effect if applied in normal doses [179]. Nevertheless, Ray et al. [191] report significant inhibition in a flooded soil by hexachlorocyclohexane (HCH) either alone or in combination with carbofuran under laboratory conditions at concentrations of 10 and 100 mg kg^{-1} soil.

Fungicides like benomyl (methyl-1-(butylcarbamoyl) benzimidazol-carbamate), dichloran (2,6-dichloro-4-nitroaniline), verdasan (phenylmercury acetate) and a number of dithiocarbamates) in normal or somewhat higher doses are sometimes effective as inhibitors of NH_4-transformation [186,271] or of oxidation of elemental S [272].

Fumigants in general and products such as methyl bromide, chloropicrin and dichloropropenes in particular effect a delay of nitrification.

This is because *Nitrosomonas* is one of the sensitive soil bacteria and part of the fumigants are applied in relatively high concentration and under cover, which results in good contact between the applied material and the soil mass.

Prasad et al. [186] list a number of compounds tested for their nitrification retarding properties. The physical and chemical properties of some of the most widely tested are given in Tabel 2.1.

N-Serve is fairly soluble in organic solvents and thus blending with nitrogen fertilizers is possible ; AM and ST have to be mixed directly with the fertilizers. As N-Serve and AM are soluble and stable in anhydrous ammonia, their use with this type of fertilizer is possible.

N-Serve (vapor pressure 0.373 Nm^{-2}) volatilizes faster than AM (vapor pressure 0.237 Nm^{-2}) and ST because the vapor pressure of the latter is lower.

Dicyandiamide, a nitrificide known as such already in the first decade of this century [32,265], and thiourea are soluble in water and can be mixed easily with, for instance, liquid manure [10].

In incubation expermiments Sommer [236] tested 57 products of the category herbicides and plant growth regulators from 11 different chemical groups for their effects on nitrifying bacteria and nitrification.

Table 2.1 Physical and chemical properties of some nitrification inhibitors.

Name (chemical trademark, manufacturer)	Melting point	Solubility			
	°C	in water g l^{-1}	in acetone kg l^{-1}	ethanol kg l^{-1}	anhydrous ammonia kg l^{-1}
2-chloro-6-(trichloromethyl)pyridine N-Serve; Nitrapyrin Dow Chemical Co	64.5	0.04 (at 20°C)	1.53 (at 20°C)	0.23 (at 20°C)	0.38 (at 23°C)
2-amino-4-chloro methyl pyrimidine	182	1.27 (at 20°C)	30.16 (at 25°C)	0.0116 (at 25°C)	0.49 (at 25°C)
Dicyandiamide Cyanoguanidine, DCD Didin	207.8	23.0 (at 13°C)	–	1.03 (at 13°C)	–
Thiourea	180.2	92.0 (at 13°C)	–	soluble	–
2 Sulfanilamidothiazole ST Mitsui Toatsu Chemicals Inc.	200.4	0.6 (at 26°C)	–	0.044 (at 30°C)	0.94 in (28% ammonia at 15°C)

None of the phenoxy compounds (mostly used as herbicides), the chlorinated aliphatic acids (e.g. dalapon and TCA) and the organophosphates used as insecticides persist in the soil longer than a few weeks and thus their effects on nitrification can be regarded as nil.

From their work with 24 compounds mentioned as more or less effective nitrification inhibitors, Bundy and Bremmer [34] concluded that 10 were so in amounts of 10 mg (active ingedient (a.i.)) per 200 mg NH_4-N. Their arrangement in decreasing order of the compounds, given as the mean of the results in three soils, is as follows:

2 chloro-6-(trichloromethyl) pyridine (Nitrapyrin) > 4-amino-1,2,4,-triazole hydrochloride (ATC) > sodium- or potassium-azide > 3,4-diamino-6-trichloromethyl-s-triazine (Cl 1580) > dicyandiamide (Dd or Dicyan or DCD) > 3-chloro-acetanilide > 1-amido-2-thiourea (guanylthiourea, (ASU)) > 2,5,-dichloro-aniline > phenylmercuric acetate > 3 mercapto-1,2,4,-triazole (MT) = 2-amino-4-chloro-6-methylpyrimidine (AM) > 2-sulfanilamidothiazole (Sulfathiazole, ST) > sodium-diethyl-di-thiocarbamate.

This order comes close to that found by Sommer [237] with compounds manufactured in the USA and Japan and mentioned as more or less specific nitrification inhibitors. With decreasing effect Sommer found:

5-ethoxy-3-trichloromethyl-1,2,4,-thiodiazole (terrazole[1]) > 2-chloro-6-(trichloromethyl) pyridine (N-Serve, Nitrapyrin) > N-2,5,-dichlorophenyl succinamide (DCS) > guanylthioura (ASU) > 2-amino-4-chloro-6-methylpyrimidine (AM) > 2-amino-4-methyl-6-trichloromethyltriazinel (MAST) and sulfathiazole (ST).

Some of these nitrification inhibitors have an effect on hydrolysis of urea as they delay the activity of urease [84]. Sommer and Rossig [239] suggest differentiation between urease inhibitors, inhibitors of the first step of nitrification ($NH_4 \rightarrow NO_2$) and those compounds working on the microorganisms that control the second step ($NO_2 \rightarrow NO_3$).

Details about urease inhibitors can be found in Ranney [189]. On the other hand urease inhibitors, as e.g. a number of quinones, have more or less specific effects on nitrifications [148].

Other chemicals have been studied and eventually developed specifically for use as a nitrification inhibitor, namely isothiocyanates [70], nitro- and haloanilines [63,64], xanthates, which inhibit both urea hydrolysis and nitrification [14], and substituted triazines. The number of these nitrificides can be appreciably extended as in the general formula 2-trihalomethyl-4-R_1-6-triazine where the halogen is chlorine or fluorine trihalomethyl, amino or methylamino can be substituted for R_1.
These triazines have, like the product MAST mentioned earlier, shown nitrification inhibiting effects.

Besides synthetic compounds, plant products such as nonedible oil seed cakes and their isolates of *Azadirachta indica*, L (Neem) and of *Pongamia glabra* Vent.
(Karanjin) are mentioned and used as nitrification inhibitors [16,214,215, 216,218,219]. Vegetable tannins [19] and waste tea, so called "tea fluff" [103] are also used, but only in the areas of origin as the amounts to be used are appriciable and the products are not easy to handle and transport.

Sahrawat [219] suggests to compare such compounds by using the "% inhibition" defined as:

$$\frac{\text{nitrification rate in control-nitrification rate in inhibitor treated sample}}{\text{nitrification rate in control}} \times 100$$

in which the nitrification rate (%) is : $[(NO_2+NO_3)\text{-}N/(NH_4+NO_2+NO_3)\text{-}N] \times 100$.
This approach is by far the most preferable for samples with relatively high contents of NH_4-4 and gives more differentiation than Bundy and Bremmers [34] : $[(C\text{-}S)/C] \times 100$ where S = amount of (NO_2+NO_3)-N in the sample with the test compound and C the amount (NO_2+NO_3)-N in the control (without test compound).

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[1] Registered trademark of Olin-Matheson Chemical Corporation (1976).

Inpurities in fertilizers (dicyandiamide and guanylurea in calcium cyanamide, biuret in urea [1]), components of industrial wastes, town refuse and combustion gases that come into soils, can inhibit microbiological processes e.g. nitrification [114]. Some of these effects have to be ascribed to the toxicity of heavy metals.

Inhibition of nitrification occurs under natural conditions [43] in grasslands or climax ecosystems [198]. Huber et al. [85], consider root exudates and compounds of decaying plants to be agents for delaying nitrification and this prevents nitrogen losses. Extracts of a luzerne-soil [112] or from the root zone of ryegrass [153] added to soil samples with NH_4-nitrogen showed some inhibition of nitrate production.

Wetselaar et al. [281] observed complete inhibition of nitrification with an osmotic value of 10 bar in the soil solution, a NH_4-N concentration of 3000 mg kg^{-1} soil and/or a pH above 8. Under more favourable conditions (lower pH, NH_4-concentrations) the process of nitrification is independent. The increase in efficiency of nitrogen by application of slow-release fertilizers or coated fertilizers [186] is partly caused by some control (retardation) of nitrification. This efficiency might be found also by applying urea and anhydrous ammonia in combination with inhibitors [72].

The inhibitors of nitrification are effective if they retard one or more steps in the following chain of reactions [72]:

NH_4 → hydroxylamin → nitroxyl? → nitrohydroxylamine → NO_2 → NO_3.

Specific inhibitors of these reactions are compounds that bind enzymes and proteins or form chelates with metals as e.g. allylthiourea, which inactivates, or oxidases containing Cu and thus restrict the oxidation of ammonia to hydroxylamine. Hydrazines inhibit the oxidation of the latter intermediate because of an effect on the transport of electrons by flavoproteins. Oxidation of nitrite is restricted or even completely inhibited by chlorates [22] as these compunds limit cytochrom c-systems.

Nitrapyrin (N-Serve) effects the oxidation of NH_4 to hydroxylamin;
3-aminotriazole, related to allythiourea, acts in a similair way.

Compounds with nitrification inhibiting properties are manufactured and selected to affect a more or less specific step in the nitrification chain.

2.2 The use of nitrification inhibitors

An ideal inhibitor should have the following characteristics [72,264]:

1. Specificity. It should block the conversion of ammonium to nitrate i.e. the activity of Nitrosomonas and be non-toxic to other soil organisms, animals and humans.
2. Mobility. It should move with the fertilizer or nutrient solution. Compounds with too high a vapor pressure may move too fast and compounds easily absorbed are probably not very effective.
3. Persistence. The material should stay active in het soil for an adequate period. Compounds cubject to rapid degradation will not be usefull.

4. Economy. The chemical should be cheap as it is used as an additive to fertilizers.

These characteristics should be tested for the purposes mentioned before (Chapter 1). These aims can be summarized as follows:

1. Prevent leaching of NO_3-N, especially in light textured soils with low water holding capacity [121] and under irrigation practices.
   If NH_4-N is applied before a period of rain it is necessary to prevent nitrification and thus leaching to secure high efficiency of nitrogen [71,75]. In this respect the application of relatively large amounts of cattle slurry in autumn or early spring in the Netherlands leads to a waste of nitrogen as nitrification and leaching of N is in no way prevented or limited.
2. Prevent denitrification of NO_3-N under conditions of bad drainage as in heavy textured soils.
3. Prevent high NO_3-contents in e.g. vegetables and forage crops.
   This aspect is important both for food quality and for fertilizers efficiency.
   Nitrification inhibitors can be mixed with solid ammonium and/or ureafertilizers or these fertilizers can be coated with the inhibitor. Application of these products in rows, bands or broadcast presents no problems. Compounds e.g. nitrapyrin soluble in e.g. liquid ammonia are useful when the fertilizer is to be injected, a practice common in parts of the USA [28,29]. Mixing water-soluble inhibitors, e.g. DCD, with slurries before application is practiced on a small scale [6,47].

2.3 The effects of nitrification inhibitors on nitryfying organisms

The number of nitrifying bacteria varies from a few thousand per gram soil in agricultural soils to some millions per gram of activated sewage sludge [273]. In climax stadia of some specific ecosystems the number of nitrifying bacteria is limited, but there are substantial amounts of NH_4-N [198]. Under conditions before the climax, relatively low NH_4-N contents were found and at the same time a higher number of nitrifiers.

In agricultural soils that are ploughed and harrowed in spring [155] aeration is improved and thus ammonification and nitrification are much stimulated, as before a crop is grown, the competition for oxygen is in favour of the microorganisms [273].

It is generallu accepted that *Nitrosomonas* spp. are the most prominent NH_4-oxidizing bacteria and that *Nitrobacter* species are concerned in the oxidation of nitrite. Bhuyia and Walker [24] and Soriano and Walker [241] found, as an exception to this rule, that *Nitrosomonas* spp. occured only in soils treated with stable manure; in other soils the ammonium oxidisers were *Nitrosocystus* and *Nitrosospira*. Heterotrophic nitrifying bacteria such as *Aspergillus flavus* species play a minor role in nitrification but these organisms are not affected by inhibitors such as nitrapyrin at concentrations up to 10 mg per litre of a synthetic medium [228].

Soil conditions, especially pH, affect the activity of the nitrifiers in as far *Nitrosomonas* is not very sensitive to pH but *Nitrobacter* spp. prefer neutral or slight acid conditions. Thus accumulation of nitrite is more likely in near neutral soils [58].

Recovery from application of one or more doses of nitrification inhibitors has not been much studied. Retardation of the process up to a few weeks or months is accepted and the effectiveness of a number of compounds has been tested in this respect [34].

According to Rodgers et al. [202] recovery took approximately 40 days from a 1 mg l^{-1} addition of nitrapyrin to aqueous suspension of different soils to which 200 mg NH_4-N per litre was added. For CS_2 the recovery was 40-60 days if a low (4 mg l^{-1}) level could be maintained. This constant level cannot be maintained easily because CS_2 is easily lost by evaporation and hydrolysis. Under such conditions recovery of nitrifying activity is rapid.

Even after prolonged incubation with both compounds no evidence was obtained for the development of nitrapyrin or CS_2 resistant nitrifiers. Recovery of nitrifiers could be achieved without addition of new bacteria.

Research with different strains of *Nitrosomonas* [286] showed remarkable differences in sensitivity among strains to nitrapyrin [107] and the conclusion of the authors is that nitrapyrin does not kill the whole population of nitrifiers. From their work with pure cultures of *Nitrosomonas, Nitrobacter* and others to which nitrapyrin was added, Müller and Hickisch [155] concluded that the reduction in the number of microorganisms is but small and cannot be the only explanation for the inhibition of the nitrification process over a relatively long period.

On the other hand Hooper and Terry [83] concluded that the effect of nitrapyrin was irreversible because they found that NO_2 or NO_3-accumulation did not recommence in their cell-free extracts after the treatments with nitrapyrin had finished. Goring [63] found the recovery better if fresh soil was added to the treated samples.

Details about the nitrification processes in soils, the effectiveness of the microorganisms involved under various conditions can be found in Lees and Simpson [111], Alexander [3], Gray and Williams [66] and Beck [21].

2.4 Effects on other (micro) organisms.

Laskowski et al. [108] found no effects of nitrapyrin and 6-chloropicolinic acid in concentrations of 1 and 10 mg kg^{-1} on 59 species of bacteria, fungi and actonimycetes. For 6-chloro-picolinic acid, mentioned as a metabolite of nitrapyrin in soils by Redemann et al. [196], up to 1000 mg kg^{-1} showed no inhibition except for *Thiobacillus thioxydans*. Some of the microorganisms involved, e.g. *Bacillus subtilis*, were retarded in their growth at levels of 100-1000 mg kg^{-1} but the effects of these concentrations on CO_2 production and soil respiration were not consistent.

Laskowski et al. [108] concluded that 6-chloro-picolinic acid does not contribute to the control of nitrification in soils. The effects of 2-amino-4-chloro-6-methylpyrimidine (AM), in concentrations up to 1000 mg 1^{-1} growth medium, on microorganisms were of little consequence [258]. Bacteria such as *Bacillus subtilis, Escherichia coli* and fungi such as *Rhizoctonia solani* and *Pythium debaryanum* were tested in pure agar cultures. Goring [63] mentioned low toxicity to fungal and bacterial poplulations whereas Müller and Hickisch [155] observed a growth stimulus for some bacterium species.

Because some inhibitors of nitrification are not very specific in their reactions, effects on one or another activity or organism in soils can be expected. Effects of inhibitors on parts of the nitrogen transformations in soils mentioned in the literature are the effects on the activity of organisms involved in biological nitrogen fixation and in denitrification. McKell and Whalley [128] found nitrapyrin nontoxic to *Rhizobium meliloti* whereas Morris et al. [285] noticed an increase in nodulation, dry weight, total N and total Ca with treatments: N-Serve 0.1 and 1 mg kg^{-1} in a pot experiment with soya beans. At concentrations greater than 10 mg kg^{-1} soil plant growth was stunted with pods failing to form. As the symptoms were not the same as those described for NH_4 toxicity, the authors explained their results through hormonal (auxin) effect.

Concentrations of N-Serve of 5 and 15 mg kg^{-1} increased the number of nodules on lateral roots of *Trifolium subterreneum* in symbiosis with *Rhizobium trifolii* [38] but decreased nitrogenase activity. Similar results were found with 2-trichloromethylpyridine (2 TMP) by the same authors but the effects were less pronounced; the variations in nitrogenase activity even unreliable. At concentrations of 50 mg kg^{-1} both inhibitors had toxic effects on root length and nodulation. This toxicity cannot be attributed to the inhibitors as relatively high NH_4-N concentrations in soils can themselves cause damage to leguminous plants [2,277].

The effects of nitrification inhibitors on denitrification were already mentioned as early as 1964 [149]. At rates of up to 50 mg kg^{-1} nitrapyrin reduced evolution of N_2O (Mills et al. [141,142], Mills and Pokorny [144, 145] and Cribbs and Mills, [51]) in soil cultures with and without plants.

According to Cribbs and Mills [51] denitrification (as N_2O loss) is more pronounced in soils with plants than in bare soils and thus the use of inhibitors might give an extra positive effect in preventing N-losses.

McElhannon and Mills [127] confirmed these findings with low ($<$ 1-2 mg kg^{-1}) levels of nitrapyrin and the retarded reduction was indicated not only by N_2O but also by N_2-gas. No explanation is given by the authors; only Mills et al. [141,142] suggest a toxic effect, at least for the high concentrations of the inhibitor, on denitrifying organisms, i.e. *Bacillus* species.

2.5 Effect on aspects of plant nutrition

The most important aspects of nitrification inhibitors and plant nutrition can be brought back to the differences between NO_3 and NH_4 as a source of nitrogen. Nitrate and ammonium behave differently in the soil. Nitrate uptake usually results in bicarbonate or hydroxyl ion excretion, and ammonium uptake causes hydrogen excretion so that the rhizosphere becomes respectively either more alkaline or more acid and this affects phosphorus nutrition and other factors [248]. Retarded nitrification thus also gives rise to differences in soil pH and these indirectly affect the activity of the microorganisms in the soil and the acidifying effects of nitrification lead to enhanced leaching of calcium, magnesium and potassium [249].

In addition to these differences which arise in soils the physiological effect of NO_3 and NH_4 on plants are most important. It is clear that species differ widely and that some, such as rice, may have a definite preference for ammonium whereas the uptake isotherms for ammonium and nitrate by ryegrass were rather similar [115]. The nitrogen status, the stage of development of the plant and the NO_3 : NH_4 ratio in the nutrient solution however affect this N uptake pattern [248]. There are also effects on uptake of other ions; nitrate tends to promote the uptake of cations, whereas ammonium sometimes increases that of anions. Different levels of organic anions are also found. That NH_4 absorption by plants suppresses the uptake of other cations has been shown by Rudert and Locascio [211] who used nitrapyrin with sweet maize and by English et al. [57] using nitrapyrin in combination with sewage sludge for maize in a pot experiment. The latter authors found at the samen time a restricted dry weight production for the treatment combinations mentioned.

Changes in nitrogen fractions in plant tissue and in protein contents were attributed to nitrapyrin by El Wali et al. [56], Sommer et al. [240] and Warren et al [275] for maize. According to the last, grain protein contents were increased from 10 to 33% but there were significant differences between soil types and in case of the mineral composition of leaves these were even more pronounced than those due to nitrapyrin. Others [37,255,257] found only minor effects of nitrification inhibitors on total nitrogen contents or N fractions in plant tissues or no effects et all. Up to now insufficient information is available to permit a full evaluation of the effects of nitrification inhibitors on grain quality as indicated by protein content and protein composition.

The effects on NO_3-contents in plant tissue mentioned in the introduction as one of the typical aspects of nitrification inhibitors will be discussed later especially in relation to horticultural crops (Chapter 6).

2.6 Research on nitrification inhibitors; critical remarks

It is easy to test the effects of nitrification inhibitors on microorganisms, i.e. bacteria, in pure cultures and under well defined conditions. Aspects of N-uptake, as NO_3-N versus NH_4-N, and the effects of water soluble inhibitors can be investigated in nutrient solution cultures under controlled conditions in growth chambers or well regulated greenhouses. But, as mentioned earlier it is accepted that the conditions in such experiments are not the same as or not even comparable with those that obtain under natural situations in the field.

Experiments with soil pot cultures and soil columns and so on are very suitable for testing the effects of nitrification inhibitors on retarding nitrification and the subsequent uptake of plant nutrients, and on the downward transport of nutrients [218,287].

An important difference between field experiment and thos in columns or pots is that in the latter the soil and the compound(s) can be mixed thoroughly so that volatilization of the compound (or of the NH_4-N) is not likely. In het field only part of the soil mass can be mixed with the inhibitor and or the feritilizer and according to Goring [64] this is a reason why the positive effects of the inhibitors in pots outnumber those in the field. The efficiencies found in pot cultures are higher. The effects of inhibitors on plants with some prefenrence for NO_3^--N are usually more marked because in pots dressed with NH_4-N + inhibitor only a little or no NO_3-N is available whereas in the field NO_3-N can be taken up from deeper in the profile.

The effects of an inhibitor can be followed be recording NO_3-N and NH_4-N in soil samples with and without the compound under consideration [176]. The amounts of NH_4-N or NO_3-N following a period of incubation soil samples with an inhibitor, expressed as a fraction of the amount added, can give a value for the efficiency of the inhibitor. Measuring either NH_4 or NO_3 can lead to different conclusions since NO_3 can be immobilized in microorganisms, leached or denitrified whereas NH_4-N can react with the organic matter of the soil or be fixed in clay particles. Beck [20] preferred measuring NO_3-N as, in his opinion, NO_3 is assimilated faster by microorganisms than NH_4-N.

Nitrification inhibitors are more effective in soil cultures, i.e. incubation experiments, because the amounts added are relatively high and also because the amounts of N in pots and applied for maximum yield are four to five times higher per kg soil than in the field [226].

In summary, an inhibitor is used under field conditions to keep the NH_4-N in the soil, preferably in the rooting zone. Some volatilization at high pH [113] and leaching of NH_4-N as found by Hendrickson et al. [74] must be taken into account. Volatile compounds, e.g. nitrapyrin, should be worked in, at least into the upper soil layers. Briggs [31] found losses of up to 80% of the compound when applied to the soil surface.

Table 2.2 Survey of literature about some aspects of nitrification inhibitors
1 General aspects of nitrification inhibitors
2 Chemical and physical characteristics of inhibitors
3 Techniques of research on inhibiting nitrification
4 Effects on nitrifying bacteria
5 Effects on other soil (micro)organisms
6 Effects on crops
  6a Yield
  6b Uptake of nutrients (chemical composition)
7 Other aspects or retarding nitrification i.e. slow release fertiliziers, urease inhibitors, soil pH
8 Effects on N-fractions in soils

Reference	1	2	3	4	5	6a	6b	7	8
Amberger and Vilsmeyer [10]		x		x					
Beck [20]			x						x
Beck [21]	x		x	x					x
Belser and Schmidt [286]			x	x					
Breteler and Smit [30]							x		
Bundy and Bremner [34]		x	x						x
Chambers et al. [38]					x				
Cox and Reisenauer [49]							x		
Cribbs and Mills [51]					x				x
Dibb and Welch [52]						x	x		
English et al. [57]					x	x	x		
Goring [63,64]	x	x		x	x				x
Hendrickson et al. [75]						x	x		
Hauck [72]	x	x							
Laskowski et al. [108]			x		x				
Lees and Simpson [111]			x	x					
Lewis and Stefanson [113]						x		x	
McElhannon and Mills [127]					x				x
Mengel and Kirkby [133]	x								
Michael et al. [137]							x	x	
Mills et al. [141,142]					x	x	x		
Mishra et al. [148]		x				x		x	
Prasad et al. [186]	x	x		x		x		x	
Ranney [189]	x	x						x	
Sahrawat and Parmar [215]	x	x		x					x
Sahrawat [218,219]	x	x	x					x	x
Sommer [236,237]			x	x				x	x
Sommer et al. [240]						x	x		
Townsend and McRae [257]						x			x
Toyoda et al. [258]					x				

Addition of some extra water, as done by Goring [64] in laboratory experiment, and in practice easy to achieve by sprinkler irrigation, is sufficient to prevent those losses. The positive effect of inhibitors in keeping NH_4-N in the rooting zone does not necessarily lead to higher yields of the crops under consideration. Nitrification may be only partially retarded or soil and weather conditions may give rise to N- losses [75]. It should be mentioned that there may even be yield depressions with crops that are not able to assimilate relatively high amounts of NH_4-N [52,99].

3 NITRIFICATION INHIBITOR NITRAPYRIN

3.1 General characteristics

Nitrapyrin is the current name of a nitrification inhibitor developed by Dow Chemical Company. It was formerly traded as N-Serve nitrogen stabilizer (N-Servefor short) and developed as DowCo 163 [63].

The active ingredient of the compound is 2-chloro-6-(trichloromethyl)-pyridine. The product can be obtained under the names of "N-Serve 24 nitrogen stabilizer" (active ingredient (= a.i.) 240 g $^{-1}$) and "N-Serve 24 E nitrogen stabilizer" (a.i. 240 g l^{-1}), the latter with an emulsifier (Dow Chemical Company, 1977).

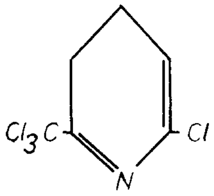


Figure 3.1.

The chemical is a white crystalline solid (molecular weight = 230.9) with a melting point of 62-63°C and solubilities in variing solvents as shown in table 3.1.

The insolubility in water has practical implications as the small amounts of the compound have to be dry-mixed with a fertilizer or must be applied directly, preferably as a solution or emulsion [263]. Application with anhydrous ammonia is practicable as regards its solubility (Table 3.1).

The compound has a relatively low vapor pressure of 0.373 Nm^{-2} (at 23°C) and this is the reason that application in spots or bands instead of broadcasting is preferred [64,263]. The rates of application advised by Dow Chemical (1977) of 1.125-2.25 l ha^{-1} of N-Serve 24 or 24E for cotton, maize sugarbeet, sorghum and wheat and of 4.50-6.75 l ha^{-1} for potatoes before or after planting or sowing are based on application in bands or rows.

Table 3.1 Solubility at 20°C of 2 chloro-6-(trichloromethyl) pyridine in different solvents. From CAJ Goring [64].

Solvent	g kg^{-1} solvent	Solvent	g kg $^{-1}$ solvent
Acetone	1940	water	0.04
Ethanol	290	anhydrous	
Toluene	1390	ammonia	400
Xylene	1120	1,1,1-trichloro-	
Methylene-chloride	1810	ethane	800

For broadcasting the rate of application has to be increased considerably [65].

Sommer [237] advises 1-10 mg per kg soil or 0.2-1.0% of the amount of fertilizer N when granulated fertilizers are used. The effects of N-Serve are focussed on the retardation of the reactions of NH_4 to NO_2 by *Nitrosomonas* spp.. Goring [63] and Shattock and Alexander [228] confirmed that only chemo-autotrophic nitrifiers are involved and that 0.2 mg l^{-1} N-Serve inhibited the growth of *Nitrosomonas europea.*

Nitrapyrin can be taken up by plants and partly decomposed in the plants. The principal residue in plants and soils is 6-chloro-picolinic acid formed by hydrolysis of the tri-chloromethyl group [196,197].

3.2 Factors effecting the effectivity of nitrapyrin

In general a chemical used to inhibit or delay nitrification and thus keeping nitrogen in NH_4-form should persist in a soil for some time. Nitrapyrin incubated with 87 soils in amounts of up to 2 mg kg^{-1} soil [63] proved to be effective in this respect as in 74 soils after 6 weeks more than 50% of the nitrogen was found as NH_4-N. It should be mentioned however that more than half the nitrogen was also found as NH_4 in 13 of the 87 soils mentioned without the addition of nitrapyrin.

The persistence of inhibitors and thus their behaviour in soils is determined by processes such as:

1. Diffusion into the atmosphere (= volatilization) of the compound.
2. Decomposition or degradation into more or less defined compounds.
3. Mobility of the compounds and especially their (differential) movement in soils
4. Sorption of the compounds on soil components such as clay and organic matter.

These processes are, with some modification according to the compound involved, the same for alle inhibitors. The factors affecting the reactions will be discussed for nitrapyrin in the following sections.

It should be mentioned that soil texture, organic matter content, pH, etc. and climate conditions have direct positive or negative effects on nitrification, whereas at the same time the effect of these factors on nitrapyrin and other inhibitors might be adverse. As an example Toughton et al [254] found little NH_4-N in an loamy soil with pH 6.8 because of enhanced nitrification and/or hydrolysis of nitrapyrin, whereas in a comparable soil with pH 5.5 both processes or at least one gave rise to large amounts of NH_4-N.

Hendrickson and Keeney [77] illustrated their findings on the effectiveness of nitrapyrin schematically as in Figure 3.2. System I illustrates a direct but incomplete effect of nitrapyrin (phase a and b) followed by a recovery of the nitrifiers (c) up to the original level. In system II addition of nitrapyrin reduces nitrification to zero (b) with a relatively slow recovery to a lower level than at the starting point.

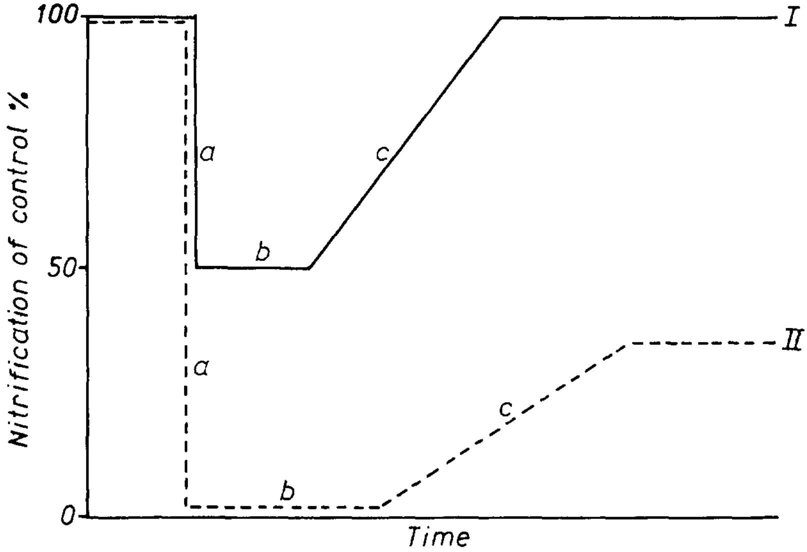


Figure 3.2 From LL Hendrickson en DR Keaney [77]

3.2.1 Texture and organic matter

In the literature on inhibitors the term "Soil type" is often used to explain results of research for which no definite cause could be found. "Soil type" is partly characterised by inorganic (sand, clay) and organic (organic matter) constituents in varying combinations. Effects on, e.g. nitrapyrin of one of the constituents are not easily separated from the effects of the other.

Goring [63,64] worked out a minimum active concentration of nitrapyrin for a number [87] of soils. In a multiple regression analysis of the logarithms of these concentrations only pH and organic matter and other unknown factors, but not clay content, accounted for the variation.

As is seen from Table 3.2 more chemical is required with increasing pH and organic matter content.

Table 3.2 Minimum effective concentrations of nitrapyrin and the average pH and organic matter content of soils. From CAJ Goring [64].

Number of soils	Minimum effective concentrations (mg kg^{-1})	Average pH	Organic matter content (%)
2	20	7.2	5.1
2	5	6.7	6.7
30	2	6.7	4.3
28	0.5	6.5	2.3
16	0.2	5.9	2.5
6	0.05	5.8	2.7

According to this author the influence of organic matter is probably due to its effect on sorption and rate of decomposition of the chemical, whereas adsorption on clay particles would not be expected as nitrapyrin has no cationic characteristics. Nitrapyrin and other inhibitors proved to be more effective in a light textured soil than in two heavier soils [34]. The halftime of degradation of nitrapyrin at 20° varied from 4 to 22 days for four different soil types [196] and from 9-16 days at 20°C for three soils according to Herlihy and Quirke [80]. All these authors mention texture and organic matter content as a possible explanation but cannot make an explicit statement about the relative importance of the two characteristics.

The conclusion of Goring [63] about the effects of organic matter and texture on nitrapyrin are confirmed by Chancy and Kamprath [39], Guthrie and Bomke [67] as regards texture and by Lewis and Stefanson [113]. The last two worked with Australian soils and found that organic matter content was not alone responsible for the effects but that in soils with a relative low C:N ratio and nearly neutral pH, and thus high nitrifying capacity, the effects of nitrapyrin are less than in soils with higher C:N ratios.

Hendrickson and Keeney [77] found complete inhibition of nitrification with nitrapyrin at 0.5 mg kg^{-1} in a soil with 1% organic matter and none in the same soil when organic was raised to 5% by adding active carbon. The same was found by McClung and Wolf [126] with nitrapyrin and terrazole when they added compost to the soil, whereas Briggs [31] observed a half life time of nitrapyrin in a sandy loam of 28 days and of 50 days in samples of the same soil mixed with peat litter over a period of years.

Sorption by organic colloids is likely to occur with nitrapyrin and according to Hendrickson and Keeney [76] hydrolysis of the chemical is not inhibited as long as the absorbed nitrapyrin is in one way or another in contact with the soil solution. On the other hand, volatilization of nitrapyrin was less in a soil with low organic C (0.68%) than in a soil with high content (3.60%) [125].

The general conclusion may be that both texture and organic matter are important in so far as heavier texture [67] and higher organic matter contents [31] have positive effects on the persistence of nitrapyrin, though both reduce efficiency.

3.2.2 pH

The influence of soil pH on persistence of nitrapyrin appears to be minimal as it had no effect on hydrolysis of nitrapyrin over the range 2.7-11.9 [76] and 3.1-8.4 [106].

The persistence of nitrapyrin in soils was not affected by pH in a sandy soil with 1% organic matter [254] but in a somewhat heavier soil with 2% and in a clay soil with 5% organic matter the nitrapyrin concentration decreased faster at high pH. Nevertheless Göring [63] showed that in soils with pH from 4.4 to 8.1 the chemical was most effective in the acid to neutral range.

The activities of micro-organisms are greatly affected by pH as was demonstrated for *Nitrobacter agilis* by McLaren and Skujms [129]. The initial population of nitrifiers and rate of recovery after treatment with an inhibitor must be related to soil pH in so far as a near neutral pH is favourable for both [273]. Hendrickson et al. [74,75] observed greater inhibition of nitrification of field applied anhydrous ammonia in a soil with pH 5.6 than in a adjacent site of the same soil with pH 7.2. It should be mentioned that these soils although of the same type differed in organic matter content and moisture conditions. Hendrickson and Keeney [77] could not confirm these results (Table 3.3.) in a field experiment with plots of one soil type maintained at pH-levels of 4.7 to 7.4 for several years.

This approach of pH-variation is preferable to amendment of a soil with acid or lime shortly before experimentation [107] as attainment of equilibria in soils takes time. The authors also ensured a high initial population of nitrifiers before addition of nitrapyrin thus avoiding effects of pre-experimental differences and enabling comparison between treatments throughout the experiment.

Tabel 3.3 The effect of soil pH and nitrapyrin (NI) on the rate of nitrapyrin (as NO_3-N in mg kg^{-1} soil per day) with NH_4-4 added at 7,14 or 28 days after application of NI. From LL Hendrickson and DR Keeney [77].

pH	Application of NH_4, days after NI								
	7 NI,mg kg^{-1}			14 NI,mg kg^{-1}			28 NI,mg kg^{-1}		
	0	0.5	1.0	0	0.5	1.0	0	0.5	1.0
4.7	2.3	2.7	2.2	4.0	3.9	2.7	3.5	3.6	2.9
5.3	6.2	5.3	4.8	6.1	5.2	5.8	8.3	6.0	5.6
5.8	6.3	4.3	3.6	6.6	4.6	3.1	7.6	5.8	6.8
6.6	7.6	4.0	2.6	7.6	4.2	3.1	11.2	4.3	4.5
7.4	7.9	0.9	0.8	15.2	6.2	1.8	11.6	7.6	7.1

According to the data in Table 3.3 nitrapyrin is relatively more effective as soil pH increases from 4.7 to 7.4. Inhibition is almost complete at pH 7.4 (treatment "NH_4 7 days after NI") but nitrifier activity recovers rapidly when the activity of nitrapyrin declines with time (14 and 28 days NH_4-N application). The authors suppose a greater susceptiblity of the nitrifying bacteria at high pH on the one hand and suggest that these organisms have a rapid recovery at this pH-level on the other hand. As various genes of nitrifiers are involved in nitrification [24] with different pH-optima, one or more dominating at a given soil pH, these results are understandable according to Hendrickson and Keeney [77].

The favourable effect of nitrapyrin at high pH in reduction of nitrification has a negative aspect as extra losses of nitrogen as NH_3 may occur [113]. These authors found a relatively low NO_3-production at low pH in accordance with the reduction of NH_4-N, but at the higher pH of calcareous sandy soils this reduction of NH_4 dit not correspond with the production of NO_3.

3.2.3. Moisture content and oxygen pressure in soils

For optimum activity of nitrifying bacteria moderate but not excessive amounts of water are necessary [36] so that aerobic conditions can be preserved. Soils differ in their optimal moisture conditions and this explains the divergent results found by Goring, who added weekly the same amount of water to a range of soil types.

Hydrolysis of nitrapyrin is enhanced in moisture saturated soils [76,109] as comparised with aerobic conditions in soils at field capacity (0.5 to 1 x 10^5 Pascal).

Movement of nitrapyrin in or eventually out of soils is related to the moisture conditions. Briggs [31] found under field conditions a slight downward movement of nitrapyrin during wet periods and and upward transport under dry conditions. Volatilization of nitrapyrin is more pronounced in wet than in dry soils [31,125]. The losses were slightest in air dry soils or when the amounts of water were sufficient to move the compound downwards into the soil [31]. McGall and Swan [125] observed enhanced losses if an air stream was passed over the soil surface.

3.2.4 Temperature

A number of research reports provide evidence that nitrification inhibitors are more effective at relatively low temperatures. Goring [63] compared nitrapyrin at 10 and 21°C against 32°C and found the compound more effective at the lower temperatures. With a number of inhibitors Bundy and Bremner [34] came to the same conclusion for all the chemicals tested at 15°C against 30°C. Hughes and Welsh [88] and Tu [262] discovered that the time period of inhibition of the nitrification is related to soil temperature and the amounts of inhibitor applied.

The above mentioned results refer mainly to laboratory incubation experiments and the temperatures with the highest effectivity of the inhibitors (e.g. nitrapyrin) are well below optimal for nitrification [100].

The decreasing efficiency of nitrapyrin with rising temperature certainly has to do with the lower persistence of the chemical in the soil and the increasing activity of nitrifiers at higher temperatures. Mullison and Norris [157] and McCall and Swan [125] found a higher degradation and volatilization at increasing temperatures (Table 3.4).

Table 3.4 Effect of temperature (°C) on volatilization (expressed as % lost) of nitrapyrin (a) applied to the soil surface or (b) incorporated at one inch depth. Air flow in the flow-through flasks was 1 litre per minute; soil moisture was one third bar moisture equivalent. From PJ McCall and RL Swan [125].

			Hours				
	Soil type	Temp. °C	0.5	1	2	4	8
(a)	Commerce	25	31	48	61	72	78
		35	53	66	77	84	87
	Barnes	25	22	33	47	59	70
		35	28	43	53	62	69
(b)	Commerce	25	8	13	20	28	37.5
		35	11	17	23	30	38
	Barnes	25	2	3	4	6	8
		35	3.0	4.5	6.4	9.0	13.5

Commerce soil: pH 7.4, organic carbon 0.68%, clay 14%; Barnes soil: pH 7.1, organic carbon 3,60%, clay 22%.

The positive effect of incorporation on persistence of nitrapyrin is clearly seen from the table, as well as the difference between the higher (Barnes) and the lower organic carbon soil. The amount of nitrapyrin lost (as a percentage) after a given time is always less in the soil with the higher organic carbon. Meikle [130] tested a simulation model for estimating the disappearance of ammonium-N from soil and had to include temperature as a variable because it affects the rate of decomposition of nitrapyrin as well as the rate of nitrification.

Half life times of 2-chloro-6-(trichloro-methyl)-pyridine (Nitrapyrin) were measured by Herlihy and Quirke [89] and they found 43 to 77 days at 10°C and 9 to 16 days at 20°C for a loamy sand and a loam. Toughton et al. [254] found 22 days at 4°C and less than 7 days at 13 and 21°C for a loamy soil with pH 6.8 and an organic matter content of 2%. In a soil with pH 5.5 and an organic matter content of 5% he found 92, 44 and 22 days at 4, 13 and 21°C respectively.

Laskowski [106] found that the rate of hydrolysis in water doubled for each 5°C increase in temperature and calculated a half life time at 25°C under this condition of 8 days. Hendrickson and Keeney [76] confirmed these results but found somewhat longer half times and suggest that temperature is more important than moisture content and organic matter as regards persistence of nitrapyrin in soils. Half life times in soils are longer since a part of the compound is absorbed to soil particles.

The results mentioned above have important practical implications as regards the time of application of the compound and its use in areas with different climates. Application at a relatively low soil temperature in late autumn or early spring has been confirmed to be positive in field experiments [27,28,44,88,176, 213]. On the other hand Toughton [253,254] found that decomposition of nitrapyrin could not be stopped at temperatures as low as 4°C and they doubt whether autumn or spring application of nitrapyrin could be succesful at soil temperatures above 13°C. This holds in particular for soils with low organic matter contents and a low pH thus with conditions favourable for nitrapyrin hydrolysis and/or decomposition.

3.2.5 Nitrogen sources

Common NH_4-N-fertilizers or chemicals were used in most experiments with nitrapyrin. Goring [63] tested $(NH_4)_2SO_4$, NH_4NO_3, $(NH_4)_2HPO_4$ and urea and found similar control of nitrification of the first three (Table 3.5).

Recovery of NH_4-N was less with urea (Table 3.5) as the fertilizer partly disappeared from the "band" before hydrolysis.

The author concluded from other data [63,64] that recovery of the nitrifiers was more rapid with urea than with the other (NH_4)-fertilizers and that nitrapyrin had no effect on the hydrolysis of urea. These findings were confirmed by Bundy and Bremmer [34] in their work with several nitrification inhibitors, among them nitrapyrin.

Table 3.5 Nitrification of solid fertilizers treated with nitrapyrin (NI) and band applied to a loamy sand[1] under leaching conditions. Results expressed as recovery of ammonium nitrogen applied in %. From CAI Goring [63].

Fertilizer	NI(%)[2]	Period after addition in weeks				
		4	6	8	12	16
$(NH_4)_2SO_4$	0	31	1	0	0	0
	1	52	24	29	23	17
NH_4NO_3	0	21	4	1	0	–
	1	52	39	36	38	–
$(NH_4)_2HPO_4$	0	30	6	1	1	0
	1	46	30	29	26	23
Urea	0	5	0	0	0	0
	1	15	9	13	7	2

[1] Sand 79%, Silt 18%, Clay 3%; pH 7.5; organic matter 0.3%

[2] As percent of ammonium or urea nitrogen

Turner et al. [263] worked with the same fertilizers that Goring used, except for urea and anhydrous and aqueous ammonia. They gave their results on control of nitrification as an avergae of the fertilizers and thus suggest no differences.

Urea and NH_3-fertilizers cause an increase in pH when hydrolysing, whereas $(NH_4)_2SO_4$ and others are acid-forming during nitrification. These higher pHs would give rise to a relatively low inhibition (3.2.4) as was found by Bundy and Bremer [34] with inhibitors such as dicyandiamide, sodiumazide and 2,4-diamino-6-trichloromethyl-s-triazine but not with nitrapyrin when they compared urea with $(NH_4)_2SO_4$. The authors suggest, in contrast to the current opinion on effects of pH, that increasing pH has a significant positive effect upon the effectiveness of different compounds acting as nitrification inhibitors in soil.

3.2.6 Other factors

In addition to those mentioned in 3.2.1 to 3.2.5 several variables effect the activity of nitrification inhibitors. Partly they are connected with management practices of soils, fertilizers and inhibitors, and most important in this respect are method and time of application. Broadcast surface application of the compound without mixing soil with the compound will require more inhibitor than incorporation in the soil or band application [31]. The low effectiveness has to do with volatilization and decomposition of the inhibitor and or differential movement of the compound and the fertilizer.

Increased effeciency may be expected when the inhibitor is applied in combination with the fertilizer as the inhibitor is in the vicinity of the

NH_4-N. The time of application interacts with temperature and moisture conditions in the soil. Generally speaking for greater activity lower temperatures are preferred [100].

3.3 Summary of research (literature)

Table 3.6 Survey of literature about aspects of nitrapyrin (N-Serve) as
1 General characteristics of nitrapyrin
2 Efficiency of Nitrapyrin affected by:
  2a Texture and organic matter content of soils
  2b pH
  2c Moisture content, oxygen oressure, tempetare
3 Nitrogen source

Reference	1	2	2a	2b	2c	3
Briggs [31]			x			
Bundy and Bremmer [34]		x	x		x	x
Guthrie and Bomke [67]			x			
Goring [63,64]	x	x	x	x	x	x
Hendrickson and Keeney [76,77]		x	x	x	x	
Herlihy and Quirke [80]		x				
Hughes and Welch [88]					x	
Laskowski and Bidlack [107]				x	x	
McLaren and Skujms [129]				x	x	
McCall and Swann [125]			x		x	
Meikle and Redemann [131]		x				
Page [176]					x	
Redemann et al. [196,197]	x	x	x			
Rudert and Locascio [210,212]		x				
Sommer [237]		x				x
Toughton et al. [254]		x		x		
Turner et al. [263]	x					x
Walker [273]				x		

4. OTHER INHIBITORS

4.1. Dicyandiamid (DCD)

4.1.1. General characteristics

The inhibitory effect of dicyandiamide or dicyanodiamide [50,58] on nitrification was already known at the beginning of this century [32,50,90,265], in Prasad et al. [186].

The compound of formula HN=C(NH_2)-NH-CN (solubility 23 gl^{-1} at 13°C; melting point 207°C; N content 67% (see Table 4.1) can be formed from calciumcyanamide ($CaCN_2$) a somewhat outmoded fertilizer. The product is manufactured from atmospheric nitrogen and calcium carbide (CaC_2).

$CaCN_2$ in water reacts to CN_2H_2 = cyanamide [246] and according tò Nommik [288] at high concentration of calciumcyamide a considerable part of cyanamide is converted to dicyandiamide. Recently Rathsack [189a] proposed a scheme for the decomposition of cyanamide in soil.

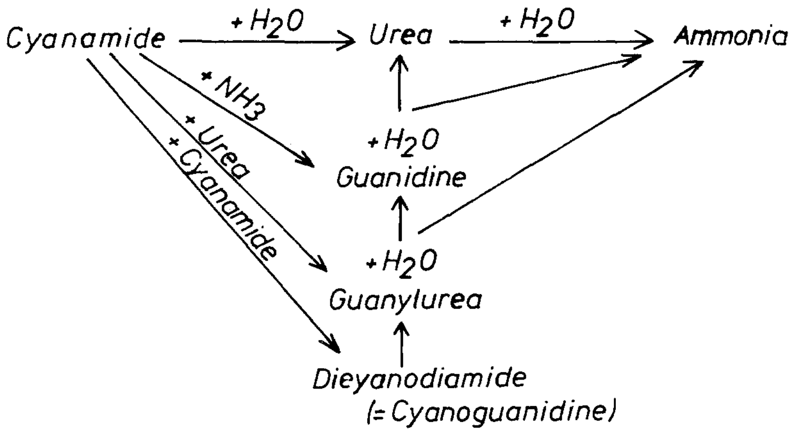


Figure 4.1 De composition of cyanamide in soil. From K Rathsack [189a].

As is seen from the scheme the formation of dicyandiamide follows via cyanamide and the compound decomposes via guanylurea into urea and or ammonia [26].

The fertilizer cyanamide ia available as a powder or in granulated form. Because of the granulating procedure these two differ in composition (table 4) in that the granulated compound contains about 10% of the nitrogen in dicyandiamide form, about 7% urea plus NH_4-N and 7% NO_3-N in addition to cyanide-N. The rate of breakdown of dicyandiamide and the formation of metabolites in the soil and the nitrification of NH_4-N is affected by these differences [268].

It should be mentioned that cyanamide itself has an inhibitory effect on nitrification, but as persistence in soil is restricted to a few weeks only, the effect is less than that of DCD, this compound being active over a period of 1-3 months.

Dicyandiamide is toxic to plants [58,193] but the effects differ with plant species.

Compounds containing urea or ammonium sulphate and dicyandiamide are available in granulated and coated form from Süddeutsche Kalkstickstoffwerke AG, Trostberg [5,232,233] and Chisso Corporation Japan [40] and recommended as slow release fertilizers.

Table 4.1 Composition of cyanamide fertilizers ; N-fractions in %.
From K Vilsmeier and A Amberger [268].

N-fraction	Powdered	Granulated
Total Nitrogen	22.85	19.42
Cyanide-N	21.85	14.50
DCD-N	0.26	1.78
NO_3-N	0.0	1.34
(NH_4 + Urea) - N	0.0	1.35
Undetermined	0.74	0.45

In most experiments, either indoor or outdoor, DCD is mixed with the nitrogen nutrient source and then mixed with the soil [192,193,194]. To bring about a good contact between the compound and the soil or quartz sand, a solution of dicyandiamid is used [7,8,9,270].

Allison et al. [4] in his toxicity studies mixed DCD, separate or in combination with sodium nitrate, with soils in respectable amounts of up to an equivalent to 44,8 kg per ha of ammonia.

A particular use of DCD has recently been studied by Amberger and Gutser [6], and Amberger and Vilsmeier [10]. They use the compound in combination with liquid cattle manure or animal slurries to prevent nitrification and thus leaching of NO_3-N especially when these slurries are applied in autumn or early spring. For the same purpose Görlitz and Hecht [289] also used N-Serve and Cooper [47] compares N-Serve, Na-azide and ATC in this respect. In an incubation experiment the latter author found N-Serve and ATC effective inhibitors of nitrification for pig slurry used in three soils with different texture and pH. Sodium-azide was ineffective, even for short periods. In a pot experiment with ryegrass and controlled percolation of the soil, DCD proved to be effective in preventing nitrification and leaching at rates of 5-10 mg per kg soil [6].

The amounts of cattle slurry used were as high as 300 mg per kg soil, the incubation temperature was 20-22°C. Amberger and Vilsmeier [10] showed, with data from another pot experiment, that 15-30 kg ha^{-1} of DCD applied with 150 m^3 $ cattle manure per ha resulted in inhibition of nitrification over 60 days at 8°C, over 40 days at 14°C and over 20-40 days at 20°C. With increasing temperature dicyandiamide was more rapidly decomposed and thus nitrification started faster after application of the inhibitor. These results were confirmed by Görlitz and Hecht [289] in as far they found effective inhibition at 20°C with 2% N-Serve or DCD (2% of total nitrogen of the manure). For DCD the effect lasted up to 3 weeks, for N-Serve up to 9 weeks. In field experiments N-Serve at 1-2% (1-2% of the total nitrogen content of the slurry) proved to be effective until March after applying cattle manure in

September of the previous year (Table 4.2). DCD was somewhat less effective but the amounts applied were as high as 8% of the total nitrogen in the manure. This is 24 kg ha^{-1} and agrees with the findings of Amberger and Vilsmeier [10].

Table 4.2 Inorganic nitrogen, in kg ha^{-1}, after application of liquid cattle manure. Manure applied on 1978-08-24, equivalent of 300 kg nitrogen per ha. Sandy soil.

	Depth (cm) of sampling	No dressing			Manure			Manure + 2% N-Serve		
		NH_4-N	NO_3-N		NH_4-N	NO_3-N		NH_4-N	NO_3-N	
1978-11-29	0–30	19	20	39	22	35	57	115	22	137
	30–60	8	13	21	5	21	26	10	14	24
	60–90	27	33	60	27	56	83	125	36	161
	0–90			120			166			322
1979-03-08	0–30	27	4	31	23	21	44	138	12	150
	30–60	8	9	17	4	24	28	7	10	17
	60–90	35	13	48	27	45	72	145	22	167
	0–90			96			144			334

The decomposition of DCD to NH_4-N [189a] must continue until the greater part of the compound has been used and the nitrifying bacteria have recovered, since the remaining part of DCD still acts as an inhibitor.

4.1.2 Factors influencing the effectivity of DCD

At a concentration of 10 mg per kg soil in three soil types and with ammonium sulphate or urea as a nitrogen source DCD proved to be less effective than nitrapyrin but was better than AM [34]. As with nitrapyrin, the effect of DCD was more pronounced in light textured soils and at relatively low temperature of 15°C. The authors found less inhibition with urea than with ammonium sulphate; for nitrayprin the reverse was observed.

Comparatively high rates of the compound are needed. Smirnov [234] found that 10-15% of the amount of nitrogen was needed to inhibit nitrification for a period of at least two months. Reddy and Datta [194] used 5 and 10 mg per kg soil to inhibit the nitrification of NH_4-N at a concentration of only 25 mg kg^{-1}.

According to Reddy [192] soil texture and organic matter content are two factors that must be considered in evaluating the length of time that dicyandiamide will be effective in any soil. He found more rapid decomposition of DCD in a sandy loam soil with relatively high organic matter content than in a coarse textured sandy soil with a low organic matter content.

He found NH_4-N after 90-150 days with DCD at least 10 mg per kg soil depending on the soil type; the amount of NH_4-N increased with increasing amounts of DCD. Adding sucrose as a quickly available carbon source for soil microorganisms, the DCD-nitrogen was utilized by the organisms thus preventing the inhibiting effect of the compound [192].

The same effect as with sucrose was found [194] when 100 mg kg^{-1} compost with 1,8% N was added to a soil. These and other factors affecting the decomposition of DCD have been studied and published in detail by Amberger and Vilsmeier [8,9], Amberger and Gutser [5] and Vilsmeier [279] following their work on decomposition of cyanamide [7,8,9,266,268,270].

DCD at 5-10% of the nitrogen was sufficient to inhibit nitrification in a pot culture with sandy loam (pH 6.1) over at least 6 weeks [5].

The same authors state that DCD is subject to leaching because they found losses of DCD up to 15% [6] in a pot experiment with liquid cattle manure and simulated percolation. The percolation, with 56 mm water was most effective on a bare soil.

According to Rathsack [189] the factors affecting nitrification by DCD are:

- the amount of DCD related to the amount of nitrogen and thus the amount of NH_4-nitrogen available in a soil or dressed.
- temperature, moisture conditions, pH and in this respect the biological activity of the soil.

Amberger and Vilsmeier [8] report that this decomposition moves very slowly in moistened quartzsand ; no changes were noticed within 100 days.

With addition of oxides or hydroxides the rates of transformation increased especially with low soil humidity. In the presence of amorphous Fe (III)-hydroxide (100 g sand and 0.5 g Fe-hydroxyde) 50% of the DCD was transformed to guanylurea within 5 days, 90% after 40 days of incubation. In the sand no NH_4-N was found at the end of the experiment. The authors suppose that the transformation of guanylurea to NH_4 which they found in two soil types, is a biological process. In these soils, a sandy loam with pH 6.5 and a sand with pH 6.3, the decomposition of DCD was somewhat slower but continued to ammonium ; 20-70% of the added DCD was transformed within 100 days.

The breakdown of DCD is accelerated with increasing temperature as is seen from the results of Vilsmeier [267] with a sandy loam (pH 6.2, organic carbon 1.09%).

The fastest breakdown is at temperatures of above 30-40°C, normally not occuring in agricultural or horticultural soils. The accumulation of guanylurea especially at this higher temperature and its decomposition via guanidine to ammonium, which is also slowed down at 50°C and 70°C, led the author to conclude that most of the guanylurea was decomposed biologically. NO_3-N was not determined. However, the results of table 4.1.2 do not suggest that appreciable amounts will be present and thus it can be expected that nitri-

Table 4.3 Effect of temperature on guanylurea and ammonium from dicyandiamide, in mg nitrogen per sample[1]. From K Vilsmeier [267]

Incubation period, days	DCD	Gu-urea	NH_4	Sum[2]	DCD	Gu-urea	NH_4	Sum
		10°C				18°C		
20	17.2	0	1.2	18.4	15.5	2	1.5	19.0
40	14.3	3	1.3	18.6	12.6	4	1.7	18.3
60	13.3	4	0.9	18.2	10.0	5	2.5	17.5
100	11.0	1	2.0	14.0	6.1	6	3.5	15.6
		30°C				40°C		
20	12.7	4	3.0	19.7	9.6	6	1.2	16.8
40	8.8	6	3.9	18.7	5.2	9	1.8	17.0
60	5.5	9	4.5	19.0	2.7	–	4.1	–
100	5.2	9	6.2	18.4	1.1	8	5.0	14.1
		50°C				70°C		
20	5.9	7	1.2	14.1	3.8	9	0.8	13.6
40	2.9	12	1.1	16.0	1.5	–	2.0	–
60	1.2	12	2.4	15.6	0.5	11	2.8	14.3
100	0.0	9	3.5	12.5	0.0	7	4.9	11.9

[1] Sample: 100 g soil + 20 mg DCD-N; soil moisture equals 40% of the maximum water holding capacity

[2] Sum = (DCD + Guanylurea + NH_4)-N

Table 4.4 Distribution of (NH_4+NO_3)-N in soil layers 0–30 and 30–60 cm (expressed as % in the 0–30 cm of the total amount of 0–60 cm) in two soils types after application of liquid cattle manure with or without DCD and N-Serve. From H Görlitz and W Hecht [289]

Liquid manure[1] with or without N-Serve/DCD		Soil type and sampling date						
		Sand (Rietz)			Loamy sand (Grosz Kreutz)			
		16-22-77	18-1-78	28-2-78	14-12-77	12-1-78	15-2-78	16-3-78
Without	53	51	49	48	17	50	47	
DCD	2%[2]	43	53	–	58	30	46	42
	4%	48	58	51	48	26	43	32
	8%	61	65	60	65	29	50	31
N-Serve	2%	87	70	76	75	63	80	69

[1] Liquid manure applied in September 1977; amounts fitting total nitrogen 300 kg ha^{-1}, NH_4-N 230 kg ha^{-1}

[2] % of the total amount of nitrogen in the cattle manure

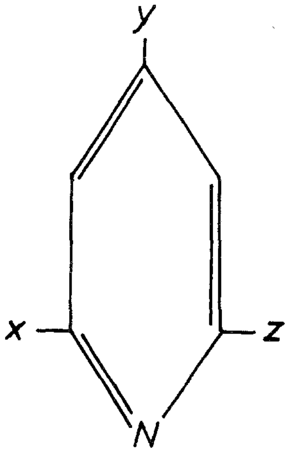
fication will be suppressed as long as DCD is present in the soil. Vilsmeier [267] estimates the inhibiting effect with 0.67 and 1.34 mg DCD-N per 100 g soil (DCD: 15-30 kg ha^{-1}) at 8°C to be over 80 days, but at 20°C only 20-40 days.

The application of DCD with liquid cattle manure has been mentioned before. Details of the work of Gorlitz and Hecht [289] are given in Table 4.4 and show a slight effect of DCD in field experiments on the sandy soil at concentrations of up to 8% DCD of the total amount of nitrogen in the manure compared with addition of N-Serve at 2% of the total amount of N.

In the loamy sand N-Serve is also more effective in preventing leaching than DCD, the more so because intensive rainfall after 14-12-77 caused substantial leaching of nitrogen from the upper 0-30 cm as is shown in treatments without inhibitor.

4.2 2-amino-4-chloro-6-methylpyrimidine (AM)

This product is one of the pyrimidine compounds listed by Ranney [189] with the general formula:



X = amino, chlorine or trichloromethyl
Y = hydrogen, amino, chlorine or trichloromethyl
Z = methyl, chlorine or trichloromethyl
(X,Y and Z are neither chlorine nor trichloromethyl simultaneously)

Figure 4.2

The product with the trade mark AM is from Toyo Koatsu Industries Inc, Japan [189,259,278] and also manufactured by Mitsui Toatso Chemicals Inc, Tokyo, Japan [258]. According to Toyoda et al. [258] nitrification inhibitors were developed in Japan for increasing crop response to urea and in 1976 the production of compound fertilizers containing AM reached 7,220 tonnes. The total production in that year amounted to about 49,000 tonnes with DD (=DCD) and ATC (4-amino-1,2,4-triazole hydrochloride) in 18,640 and 11,038 tonnes respectively.

Purified AM is a white crystalline substance with a melting point of 182°C. The technical product is a yellowish brown powder with some impurities. The compound is soluble in water and anhydrous ammonia but, unlike nitrapyrin, relatively insoluble in organic solvents such as acetone and ethanol. As AM is stable except at $pH = 4$ or less, it can be applied with almost any kind of fertilizer [258]. However the compound should not be kept for long in association with acid fertilizer materials [186,187]. The vapor pressure of $0.237\ N\ m^{-2}$ makes it preferable to coat AM onto the (compound) fertilizer at a temperature of 35°C or less. Losses of AM are negligible as 95% of AM remains when a AM-fertilizer is stored in a polyethylene bag of 0.1 mm thickness for a year at 30°C.

Effective rates of AM of 5-6 kg ha^{-1} mixed with fertilizers are given by Prasad et al. [186] for retarding nitrification of urea. In field tests with rice under waterlogged conditions with urea as a fertilizer 4-10 mg kg^{-1} soil proved to be effective [89,188]. The inhibition period was generally not longer than 20 days to one month. According to Smirnov [234] 0.5-2% of the amount of nitrogen should be used whereas Sommer [237] advises 2-10 mg kg^{-1} soil of the active compound or 0.5% for coatings on fertilizer granules.

The duration of the nitrifying effect is 3-4 weeks at 2-5 mg kg^{-1} soil [258]. These authors emphasize that both AM and ST (=sulphathiazole), the compound they used under comparable conditions, have no effect on ammonification of urea and do not inhibit the conversion of nitrite to nitrate even at a concentration of 100 mg kg^{-1} soil.

Comparing nitrification inhibitors Rajale and Prasad [188] and others found AM as effective as N-Serve in their experiments with ammoniacal fertilizers and rice as test crop. Bundy and Bremner [34,35] found that AM was less effective than nitrapyrin and DCD whereas at 30°C the inhibiting effect of AM was less than at 15°C. This effect of temperature is also mentioned by Toyoda et al. [258].

In moistened samples of five soils with clay contents of 15 to 67%, organic matter of 1.7 to 3.2% and pH between 5.0 and 6.2 Weir [278] incubated AM at rates of 20 mg per kg soil. Samples were taken at regular intervals over a period of up to 40 days and extracted with an acidified (pH 3) 10% KCl-solution for determination of residual AM. The amount if inhibitor remaining in treated soils was logarithmically related to time. This relationship is clearly influenced by the cation exchange capacity and the surface area of the soil constituents in as far as in heavy textured soils less AM is extracted. The author suggested that adsorption by soil colloids is the predominant process by which the inhibitor is immobilized but does not exclude that some part of the compound is decomposed by microorganisms.

As no difference was found in extracted AM-contents from samples incubated in open or closed pots volatilization of AM can be neglected. With AM at 20 mg per kg soil and at moisture contents equivalent to air dry, half of field capacity and field capacity Weir [258] concluded that in the wetter samples more of the AM was fixed.

4.3 5-ethoxy 3-trichloromethyl-1,2,4-thiadiazole (Terrazole)

5-ethoxy-3-trichloromethyl-1,2,4-thiadiazole is the active compound of a material developed by Olin Corporation, Baltimore, USA, and registered as "Terrazole^r, soil fungicide". Other trade marks of the active component are Pansoil^r, Truban^r, Koban^r and Aaterra^r. As a nitrificide the compound is the active ingedient of "Dwell^{tm} nitrification inhibitor" [173]. The structure, as shown below, classifies the compound in a group of thiadiazoles.

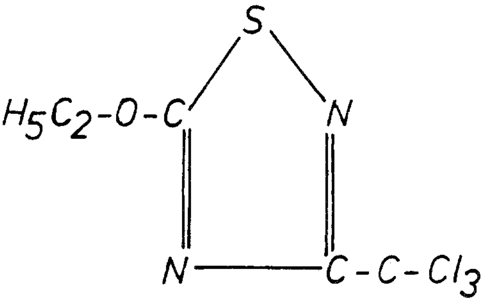


Figure 4.3

The product is available [264] as a wettable powder or technical grade liquid with 35% and 95% active ingredient, respectively. As a coating on ammonium sulphate and urea fertilizer terrazole, 95% ai is used up to 1,5% by weight [174]. Because Terrazole^r has a vapour pressure, as nitrapyrin, of 1.33×10^{-2} N m^{-2} at room temperature, incorporation into the soil after application is favourable.

Rates of application advised by Olin corporation [173,174] are 0.6-1.1 kg ha^{-1} for crops like potatoes, sugarbeet, lettuce and onions.

The nitrificidal properties of Terrazole^r were first reported by Sommer [237] after his findings of complete inhibition for 56 days of incubation with 1 mg kg^{-1} soil of the compound and for 84 days with 5 mg kg^{-1}. Further research on the persistence of the compound was done by Olin corporation [173,174], Turner and Macgregor [264] and McClung and Wolf [126].

Amounts of ammonium sulphate, equivalent to 226 kg nitrogen per ha, uncoated and coated with 0.5 or 1.0% Terrazole^r (Dwell^{tm}) were incubated with a silt loam (pH 6.6 ; organic matter 3-3.5%) for up to 12 weeks. Measurements at 18°C of NO_3-and NH_4-N conversion started 3 weeks after incubation and was completed after 9-10 weeks. For 1.0% Terrazole^r the comparable figure were 7 and 9-10 weeks respectively [173,174]. In a second experiment 2-25 mg kg^{-1} soil of the compound retarded nitrification for 8 weeks ; 1 mg kg^{-1} soil held ammonium only for 4 weeks whereas without Terrazole^r the nitrification of 200 mg nitrogen per kg soil, as ammonium-sulphate, was completed after the same period. Amounts of 5 and 10 mg kg^{-1} soil prevented any nitrification of NH_4-N for a period of at least 10 weeks.

Turner and Macgregor [264] incubated 1 g N per kg substratum as Terrazole-coated urea (1% coating) or mono-ammonium phosphate (10% coating) in a 1:1 mixture of a silt loam with acid washed sand.

As can be seen from the results (Table 4.5) at the end of a relatively short incubation period nearly 46% of the incubated urea and 22% of the uncoated mono-ammoniumphosphate had been nitrified whereas Terrazole-coated fertilizers gave negligible amounts of NO_3-N.

The same authors concluded from experiments in which a nutrient solution containing NH_4-N with or without Terrazole was percolated through a soil column that the nitrate production in the leaching solution was reduced to zero within two days and that the compound moved through the soil column. The Terrazole concentration used was 0.1 mg l^{-1}. McClung and Wolf [126] showed a lower efficiency for Terrazole^r as well as for nitrapyrin when compost was added to the substratum.

Table 4.5 Nitrate formation (NO_3-N in mg kg^{-1} soil) in soil samples receiving Terrazole-coated and uncoated urea and coated mono-ammoniumphosphate.
From MA Turner and AN Macgregor [264]

Treatment	Days of incubation		
	9	19	29
Urea	88	95	457
Urea + Terrazole	1	1	4
Mono-amm. phosphate	19	35	219
Mono-amm. phosph. + Terr.	1	1	1
No fertilizer	3	1	1
Terrazole only	1	5	8

4.4 N-2,5-dichloro-phenyl-succinamic acid (DCS)

The active compound of the above mentioned inhibitor is 2,5-dichloroaniline (DCA) produced from DCS by hydrolysis [163]. But DCA cannot be mixed with fertilizers such as urea or nitrophosphates [163] because of its high vapor pressure. The hydrolysis is accelerated by higher temperatures but can be depressed by some fungicides [164] so that microorganisms possibly play a role in this hydrolysis.

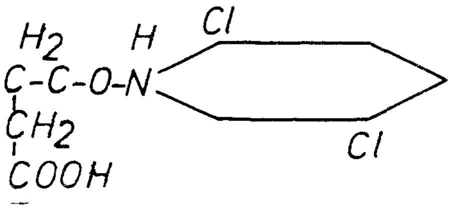


Figure 4.4

Effective amounts of 10-20 mg kg^{-1} soil or 0.3% of the amount of nitrogen for coated fertilizers were used by Namioka and Komahi [162] and Sommer [237]. The latter author found no effect on *Nitrosomonas* culture probably because of volatilization of the compound but incubation with 5 mg DCS per kg soil retarded nitrification of NH_4-N for 56 days and rates of 10-20 mg kg^{-1} soil were effective for 84 days, when the experiment ended.

Sampei and Fukushima [221] used high rates of 3-20% on the applied nitrogen basis for 17 chemicals, DCS included. Dwarfing and reduced fresh weights of kidney beans were noticed with this compound; the effect seemed to be apparant only in leguminous crops. According to Bundy and Bremner [34] 2,5-dichloroanaline was not effective regardless of the soil type at a temperature of 30°C. At 15°C the inhibition of nitrification was 13 and 57% for soils with 5.0 and 3.5% organic carbon respectively, while for nitrapyrin under the same conditions the comparable figures were 87 and 94% and for DCD 69 and 71%. According to Namioka and Oshio [164] adsorption on soil colloids, especially in soils with substantial amounts of organic matter explains the lower efficiency and decreasing leaching of the compound with increasing organic matter.

4.5 Non synthetic nitrification inhibitors

The foregoing chapters have dealt with synthetic nitrifications inhibitors. These compounds are relatively expensive and are not available in a number of countries. Naturally occuring materials mostly of vegetable origin have been tested and used e.g. in India to increase the efficiency of fertilizer nitrogen [161].

These products contain small amounts of nitrogen and had been used as manure in the past before their nitrification inhibiting properties were known. In the following sections some of the work with "Neem" (4.5.1), "Karanjin" (4.5.2), and "Mahua" (4.5.3) is discussed.

4.5.1 Neem

"Neem" or "Margosa" is an indigenous tree (*Azadirachta indica* L.) described by Chopra et al. [42] from India with non-edible oil-bearing seeds. "Neem" (and also "mahua")-cakes were used as a manure but their value was inferior to that of in organic fertilizers. The presence of bitter and odoriferous substances, mainly nimbinan acrid alkaloids [159], was given as an explanation for this inferior quality [16].

"Neem" cake is mixed or blended with the fertilizer, mostly urea; alternatively extracts of the oil cake with acetone, pertroleum-ether or alcohol are supposed to have nitrification inhibiting effects and are incorporated into the soil [16,59,98,122,146,147,159,160,187,195,215,227,231,244,266,290]. Patil [180] used "Neem" oil and the three major fractions, viz. total bitters, sulphur-containing odoriferous compounds and pre-refined oil in an incubation experiment. The maximum inhibition of ammonium nitrification after 30 days of incubation was found with 12% "Neem" oil (12% of the amount of nitrogen). Among the fractions, the bitters were together mainly responsible for the inhibiting effects.

Urea treated with an acetone extract of "Neem" seed crush gave higher yields for rice [16] and was more effective than slow release urea compounds or untreated urea at a level of nitrogen of 100 kg ha^{1}. An alcohol extract of "Neem" was used by Sahrawat and Parmar [215]. In their experiment a dosis of 30% extract (based on NH_4-N) gave higher NH_4-N contents in a soil treated at 30°C with nitrogen at 200 mg kg^{-1} as ammonium sulphate or urea after 75 days of incubation. The amounts of "Neem" cake applied differ widely. Mishra et al. [147] based the calculated amounts of "Neem" cake powder on the C content of the product. With a C-content of the cake of 54,8% and 0,2%C as an effective amount the equivalent portion per ha comes to 8156 kg. This amount will undoubtly assist in building up soil organic matter.

Shanker et al. [227] found positive effects in a field experiment with 20-40 kg ha^{-1} "Neem" cake in combination with nitrogen at 100 kg ha^{-1} as urea for rice as a test crop. With the same amounts Mishra and Chhonkar [290] found retardation of nitrification for up to 160 days in an incubation experiment at 28°C.

4.5.2 Karanjin

A number of physiologically active compounds belonging to the group of furano-flavonoids are found in seeds, bark and leaves of the tree *Pongamia glabra*, Vent., known as Karanja [291]. Their nitrification inhibiting properties were mentioned as early as 1953 and 1966 [229].

Sahrawat et al. [214] tested alcohol extracts of seeds, extracts of the bark and ground leaves of the tree in an incubation experiment with a sandy loam (pH 7.7; organic-C 0.6%) and 200 mg nitrogen per kg soil as ammonium sulphate or urea. They confirmed the characteristics mentioned in as far as retardation of nitrification was obvious with seed and bark extracts though leaves and their extracts showed no effects. 10% of nitrogen added as ammonium sulphate without inhibitor was present as NH_4-N after 60 days, but when 30% (based on amount of nitrogen) seed or bark extract was also applied this percentage was 23 and 20 respectively.

"Karanjin" is the principal furano-flavonoid and can be isolated from karanja seeds and oil but a number of related compounds are also isolated, and these have been thoroughly investigated and used as medicine, nitrification inhibitor and cattle feed [216,217,220,291].

According to Sahrawat and Mukerjee [216] the activity can be ascribed to the furan ring in Karanjin because, dihydrokaranjin with a reduced furan ring has no inhibiting properties (see scheme below).

Karanjin (3-methoxy furano-2',3',7,8-flavone) (I) was isolated from karanja-seeds and -oil. Karanji ketone (4-hydroxy-5-w-methoxyacetyl coumarone (II) and karanjonol (3-hydoxy furano-2',3',7,8-flavone (III) were prepared from karanjin.

Dihydrokaranjin (3-methoxy dihydrofurano-2',3',7,8-flavone (IV) prepared by hydrogenation of karanjin, was obtained as colourless needles (m.p. 187°C) from an ethanol extract. Formula $C_{18}H_{14}O_4$ would have 73.5% C and 4.7% H, values found were 73.4 and 4.5% respectively.

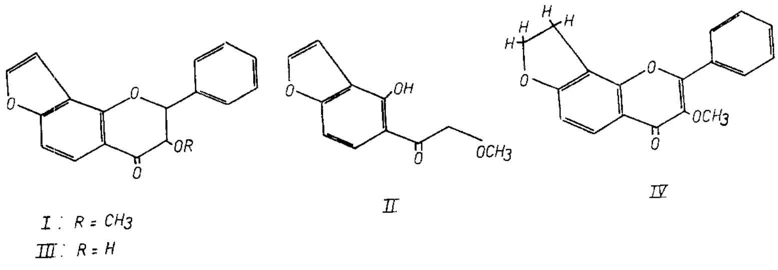


Figure 4.5 Structural formulae of the test compounds: – I, Karanjin: II, karanjeketone; III, karanjonol; and IV dihydrokaranjin. From KL Sahrawat and SK Mukerjee [216]

The authors concluded from tests with rice in pot culture experiments that Karanjin could compete with N-Serve (Nitrapyrin) for a period of up to 5 weeks and at amounts of 5% of the NH_4-N added as $(NH_4)_2SO_4$ or urea.

After 5 weeks the performance of N-Serve was slightly better than that of Karanjin. For both treatments the amounts of NH_4-N in the soils were higher for up to 8 weeks, the duration of the experiment, as compared with control.

As no nitrite was found with either chemical (N-Serve or Karanjin) they concluded that nitrite oxidising bacteria were not inhibited.

In further research work Sahrawat et al. [217] prepared and screened more furano compounds to search for effective and cheap inhibitors. Compounds such as furfural and furfuryl alcohol were effective in inhibiting nitrification at 10% of NH_4-N and higher rates of application (see Table 4.6).

The authors suggest a significant improvement of the inhibiting effects by preparing urea-furfural compounds.

Table 4.6 Effects of furfural and furfurylalcohol as compared to Karanjin on nitrification in soil treated with ammonium sulphate (AS) and urea.

Inhibitor	Fertilizer	Nitrification rate[1] after days				
		15	30	45	60	75
None	AS	17	44	73	86	94
	Urea	19	45	74	87	94
Karanjin,5%	AS	6	17	39	62	86
	Urea	6	15	40	60	83
Furfural,10%	AS	7	28	67	74	89
	Urea	6	15	68	84	93
Furfural,30%	AS	5	8	13	48	81
	Urea	3	5	25	76	92
Furfuryl-alcohol,10%	AS	7	15	61	68	89
	Urea	13	27	67	84	93
Furfuryl-alcohol,30%	AS	3	6	18	46	86
	Urea	7	8	25	76	93

[1] nitrification rate $= \frac{(NO_2 + NO_3)\text{-N}}{(NH_4 + NO_2 + NO_3)} \times 100(\%)$

4.5.3 *Mahua*

According to Bains et al. [16] "mahua" (= *Bassia latifolia*, Roxb) also mentioned ad *Madhuca indica* Gmel [62] extracts containing saponin could be responsible for slow mineralization of nitrogen. Göhl [62] gives the name "mahua" "mee" or "illipi" for *Madhuca longifolia*, L.

In an incubation experiment with clay loam, amounts of nitrogen of 50 and 100 kg ha^{-1} as urea and six indigenous nitrification inhibitors with "mahua" cake extract, Muthuswamy et al. [160] found no inhibiting effects after more than 20 days incubation. "Neem" cake extracts did not show very promising effects in this study.

4.6 Other inhibitors

A number of organic chemicals other than those discussed in the foregoing chapters have been mentioned as nitrification inhibitors [34,189].

Thiourea and a number of derivates of this chemical, e.g. 1-amidino-2-1-thiourea, were tested [189,186] especially for rice and shown to be effective under certain conditions [186].

A group of thiazoles, such as sulfathiazoles and especially 2-sulfanilamidothiazole (ST) were introduced as nitrification inhibitors by Mitsui Toatsu Chemicals, Inc. Japan [186]. General properties of ST were described by Toyoda et al. [258] and Toyo Koatsu Ind. [260]. In their incubation tests with both chemicals in concentrations of 2-5 mg per kg soil ST was more effective than AM in volcanic ash soils. AM was seen to be more effective than ST in alluvial soils. Bundy and Bremner [34] found only a slight effect on nitrification when compared with products as Nitrapyrin and DCD.

At concentrations of up to 20% of the applied nitrogen ST caused severe damage to kidney bean and chinese cabbage [221]. 4-Amino-1,2,4-triazole (ATC) belongs to the amino triazole group, a group of nitrification inhibitors described by Ranney [189] some of which were tested by Bundy and Bremner [34]. In a series of field experiments with silage maize and with urea broadcast or banded the compound was shown to be more effective than N-Serve [67]. Bundy and Bremner [34] classified potassium and sodium azides in the group of the most potent nitrification inhibitors. Potassium azide (KN_3) applied in field tests with anhydrous ammonia in fall and spring in 1970, 1971 and 1972 and compared with N-Serve showed inhibiting properties [99], The results varied from year to year and positive results of the inhibitor on yield of maize were only observed in one of the experimental years.

Carbon disulphide (CS_2) was found extremely effective for inhibiting the action of bacteria responsible for ammonium oxidation. In open jars the compound evaporates rapidly and is thus not effective [11,12]

However, CS_2 can be generated from trithiocarbonates and application of these compounds is possible as they are not volatile, inflammable and less offensive than CS_2. Asworth et al. [11] found CS_2 particularly effective compared to nitrapyrin when incorporated in bands with aqueous ammonia or urea solutions. As is already known nitrapyrin persists in soils for a long period but its movement from the band of application is limited.

On the other hand, CS_2 diffuses from the injected band rapidly and causes inhibition of nitrification in a large volume of soil but has short persistance and no residual effects. According to the authors the period of inhibition, depending on the temperature-dependant speed of recolonisation of nitrifiers, is long enough to prevent leachting and denitrification of NO_3-N during winter when the nitrogen is dressed in autumn.

Diethyl-di-thio-carbamate is mentioned as an inhibitor of oxidation of NH_4 by *Nitrosomonas* spp because the compound inhibits Cu containing enzymes [110]. Of the group of non-synthetic compounds Jain et al. [91] mentioned and tested "Citrullus coldsynthis" cake for wheat.

4.7 Summary of research (literature)

Tabel 4.7 Survey of literature on DCD and other nitrification inhibitors (expect nitrapyrin)
1 DCD, general
2 Factors influencing the effectivity of DCD
3 Other synthetic inhibitors
4 Non synthetic inhibitors

Reference	1	2	3	4
Amberger abd Gutser [5]	x	x		
Amberger and Vilsmeier [8,9]	x	x		
Bains et al. [40]				x
Bundy and Bremner [34,35]			x	
Chisso Corporation [40]			x	
Gasser [58]	x			
McLung and Wolf [126]			x	
Nair and Sharma [161]				x
Namioka and Komahi [163]			x	
Namioka and Oshio [164]			x	
Olin Corporation [173,174]			x	
Parmar et al. [291]				x
Patil [180]				x
Prasad et al. [186,187]			x	x
Ranney [189]			x	
Rathsack [189]	x			
Sahrawat [220]				x
Sahrawat et al. [217]			x	x
Sahrawat and Parmar [215]				x
Sahrawat and Mukerjee [216]				x
Sampei and Fukushima [221]			x	
Sommer [237]			x	
Süddeutsche Kalkstickstoffwerke (SKW) [232,233]	x	x		
Toyoda et al. [258]				
Turner and McGregor [264]			x	
Vilsmeier [266]		x		
Vilsmeier and Amberger [268,269]		x		
Weir [278]		x		

5 EFFECTS OF NITRIFICATION INHIBITORS ON AGRICULTURAL CROPS

Classifying literature on nitrification inhibitors under various crop headings may not be the most reasonable thing to do. The effects of the inhibitors are mostly noticeable and measurable in the soil, their effects on plants being indirect, for instance because of their distinct sensitivity to ammonium nitrogen. On the other hand the different behaviour of crops in response to type of nitrogen can give a basis for a classification based on crops. In the following, literature on inhibitors is presented for cereals (wheat 5.1; maize 5.2; oats 5.3); potatoes 5.4; grassland 5.5; and other agricultural crops 5.6).

5.1 Wheat

Nelson et al. [167] and Boswell et al. [26,27] conducted several trials with winter wheat in the southeast of the United States (Virginia, Georgia, Tenessee) and compared nitrogen dressings in autumn and or spring with and without addition of nitrapyrin. The conclusions of this and other unpublished research results are summarized by Toughton and Boswell [256].

The inhibitor was effective until January but at the time of the most important growth of wheat (winter wheat) in March no differences in NH_4-N contents in the soils with and without nitrapyrin were found. The authors suggest that, owing to the mild climate, the persistence of nitrapyrin is of short duration and not effective for NH_4-N applied in autumn or early spring. So the highest yields were found with split applications of nitrogen (one third in autumn and two thirds in spring).

In the Mid-West of the USA, in the so-called corn belt, many studies have been made on the prevention of losses of nitrogen by using nitrification inhibitors. The results for the eastern part of the Midwest (Illinois, Kentucky, Michigan, Ohio and Wisconsin) are summarized by Nelson and Huber [168], those of the western part (Nebraska, Kansas, Colorado and Minnesota) by Hergert and Wiese [79]. For wheat, in 21 out of 24 comparisons of urea and anhydrous NH_3 with and without a nitrification inhibitor (Nitrapyrin was used in 21 and Terrazole in 3 of the comparisons) the first authors found yield increases averaging from 9.9% in 1974 to 24.1% in 1976. The best results of the inhibitors were obtained on all soil types with applications of nitrogen before planting in spring whereas when N was side dressed in spring inhibitors were ineffective as there is opportunity for N losses in the short period between application and uptake. On sandy soils the inhibitor may be especially effective as these soil types are subject to leaching.

Yield responses to nitrification inhibitors, mainly nitrapyrin, are found mostly in the southern area of the midwest as in the northern part lower winter temperatures and somewhat lower rainfall reduce leaching. The authors subscribe to the view that negative or zero responses to inhibitors can be expected with soils having high levels of plant available nitrogen and during seasons and with soil types having little or no N losses as might be caused by below average rainfall or heavy soil texture. Also with N dressings far in excess of those required for maximum yield no effects of inhibitors can be expected.

In the western part of the midwest winter and early spring rainfall is generally insufficient to leach nitrogen below the rooting zone and as denitrification is also minimal little improvement may be expected from the use of nitrification inhibitors in dry land crops [79]. According to these authors inhibitors may have some effect on irrigated sandy soils particularly when erratic rainfall follows irrigation as can be expected in the part of this area called the Great Plains. Nitrification inhibitors proved to be effective in delaying nitrification in field and incubation experiments in this area as was demonstrated by Janssen [92], and Hergert et al. [78] with Nebraska soils, by Bundy and Bremner [35] using Iowa soils by Moraghan and Albus [154] with soils of North-Dakota and by Malzer [121].

Harrison et al. [71](found a positive effect on yield of winter wheat whit a fall application of nitrogen (anhydrous or aqueous ammonia, injected) and nitrapyrin on silt loam (loessial) soils of Washington State, USA. Other authors [177] also showed that nitrapyrin at rates of about 0,5 kg ha^{-1} was effective in decreasing nitrification of anhydrous NH_3 during a fallow period in the Pacific Northwest (Washington, Idaho).

Also potassium azide (KN_3) was effective as a solution with anhydrous NH_3 as long as no leaching occurs. Leaching makes KN_3 ineffective as the chemical is removed from the application zone.

Tabel 5.1 Yield (kg ha^{-1}) of winter wheat affected by urea[1] and anhydrous NH_3[2] with and without nitrapyrin.

N applied (kg ha^{-1})	Urea - nitrapyrin	Urea + nitrapyrin
67	5443	5376
134	5107	6653
268	6115	7258
	NH_3 - nitrapyrin	NH_3 + nitrapyrin
0	3427	
34	4570[a]	4750
90	5309	5645
180	5914	6115

a) None of the yield differences are significant at the 0.05 probability level.

1) From TH Chaudhary (1966). The effect of nitrogen source and 2-chloro-6-(trichloromethyl) pyridine on the nitrogen and sulphur nutrition of wheat. Ph.D. Thesis Washington State Univ. Cited by Papendick and Engibous [177]

2) From VL Cochran, RL Warner and RJ Papendick (1977). Effect of nitrification inhibitors and depth of applied N on yield and protein content of winter wheat, In : Proc 28th Annual Northwest Fertilizer Conference Twin Falls Idaho, 53-61. Cited by Papendick and Engibous [177]

Crop response to nitrapyrin in the area mentioned has not however been as consistent as is shown in Table 5.1. Under the wheather conditions of the northwest with rainfall of 250-600 mm, plants (without irrigation) have to find their water in the deeper layers from May onwards. If at the same time the bulk of the nitrogen is kept in the upper soil layers, i.e. by inhibition of nitrification, lower yields and reduced N-efficiency could result [177], especially if N uptake during grainfilling is important for high protein content [45].

From his work in the field and in growth chambers with nitrapyrin and nitrogen dressing on spring wheat in Manitoba, Spratt [242] concluded that the use of the inhibitor had no effect on yield (grain and straw) and on nitrogen, phosphate, and potassium contents of the crop. The relatively high NH_4-N contents in the soil at the beginning of growth had a beneficial influence on development of the yound wheat plants.

The author used urea and ortho- and polyphosphates of ammonia as fertilizers.

More recently, improved yields of cereals were found in Alberta, Canada with fall applied nitrogen plus inhibitors [172,118,119], cited by Ashworth and Rodgers [13].

Sommer et al. [240] compared, for winter and spring wheat, a commonly used dressing system with split application of nitrogen of 120-200 kg ha^{-1} as ammonium nitrate limestone and an injection of 120-300 kg ha^{-1} as ammonia with nitrapyrin in field trials on loam and sandy loam soils in West Germany. They conclude that injection of NH_4-N + nitrapyrin gives equal grain yields to split dressings. The relative high amounts of nitrogen given as ammonia caused no yield depression.

Under the climatic conditions of central Europe (Czechoslovakia, German Democratic Republic) Matzel et al. [123] found no differences in losses of nitrogen from fall applied ammonium sulphate labelled with ^{15}N with and without N-Serve (nitrapyrin) under low fall temperatures and low precipitation during the winter period. With higher temperatures in autumn and much winter precipitation 69% of nitrogen was lost without N-Serve and only 28% with addition of N-Serve at 2% of the amount of nitrogen on a loam soil (pH 6.8).

Lewis and Stefanson [113] used N-Serve with $(NH_4)_2SO_4$ on Australian soils, some frequently cropped in a wheat-fallow rotation, others under pasture for 16 years before wheat cropping. The concentration of N-Serve on "pasture" soils had to be up to 5% of the amount of N to get the same inhibition of nitrification as on the others with 0.2% of N-Serve. This difference is related to the effects of organic matter on effectivity of nitrapyrin as was seen above (3.2.1.). Under field conditions the inhibitor was found to have no effects on yield and N-uptake of wheat ; however, $NaNO_3$ gave higher yields than the NH_4-fertilizer with or without N-Serve (Table 5.2)

Table 5.2 Yield of grain and total yield of wheat (kg ha^{-1}); Nitrogen uptake (kg ha^{-1}) on Urrbrae red-brown earth soils. N: 112 kg ha^{-1}; N-Serve 10% W/W NH_4-N.
From DC Lewis and RC Stephanson [113]

Treatment	Urrbrae-pasture			Urrbrae wheat-fallow		
	Grain	Total	N-uptake	Grain	Total	N-uptake
Control	2019	7537	52.0	1194	4981	32.8
Control + N-Serve	1621	7211	41.4	1253	5033	38.6
$NaNO_3$	2092	10987	67.1	1624	7935	54.6
$(NH_4)_2SO_4$	1508	9813	63.7	1331	7530	45.6
$(NH_4)_2SO_4$ + N-Serve	1676	10095	70.7	1327	7595	46.8

Osborne [175] showed that on New South Wales soils, Australia a dose of N-Serve of up to 10 mg per kg soil was not phytotoxic as indicated by wheat dry matter yield after 60 days of growth and grain yield at harvest. At the 10 mg per kg level of inhibitor maturity of wheat was signigicantly delayed.

Some of the research work on nitrification inhibitors in the Union of Soviet Socialist Republics (USSR) is summarized by Smirnov [234].

Yield increases of 5.5-8.0% were found with N-dressings of 60-90 kg ha^{-1} and N-Serve at 0.5-1.0% to unirrigated winter wheat and irrigated spring wheat.

5.2 Maize

The effects of nitrification inhibitors on fall-applied nitrogen for maize are comparable to those for wheat as far as these effects are found in differences in amounts of NH_4- and NO_3-nitrogen in the soil. Limited available data indicate that nitrapyrin will delay nitrification under the climatic conditions of the south east of the United States [256] but as the soil temperature is relatively high the persistence of nitrapyrin is short (3.2.4).

Nitrapyrin was found to have no effect on yield or chemical composition of maize in a number of experiments and demonstrations testing nitrapyrin with urea, anhydrous ammonia and nitrogen solutions [28], but in the state of Maryland and Georgia there were considerable yield increases (data from GM Lessmann for Maryland and DB Hale for Georgia, mentioned by Thoughton and Boswell, [256]) and explained by Thoughton and Boswell as being related to relatively low temperature and excessive rainfall during the early growth period. With heavy rainfall during the growing season, Huffman, Hale and Lessman, mentioned by Toughton and Boswell [256], reported substantial yield increases for maize with nitrapyrin as a nitrification inhibitor in field trials and growers demonstrations in south east USA and Prasad and Turkhede [185] in India obtained similar results.

Other experiments with maize were done on soils with poor drainage [253,99] so that leaching of nitrogen is not expected or under climatic conditions unfavourable for leaching [75] so that effects of nitrification inhibitors are not likely. On the contrary, on irrigated coarse sands Malzer [120] found a yield increase with nitrapyrin and terrazole combined with urea (N:60-240 kg ha^{-1}). These treatments did however not augment yield as compared with nitrogen applied in four splits. The results found by Toughton et al. [253] with anhydrous ammonia plus nitrapyrin in 1975 and 1976 in Illinois were not consistent among N rates, locations and years. Under some conditions, i.e. with nitrapyrin at 1.12 kg ha^{-1}, N-concentration in tissue samples was increased.

Nevertheless, Toughton et al. [255] conclude that nitrapyrin-treated urea is not needed for maize production in Illinois, USA. In the experiments of Hendrickson et al. [75] in Wisconsin nitrapyrin inhibited nitrification considerably, so that still in May more than 50% of fall-applied, banded, anhydrous ammonia was available as NH_4-N, whereas in a comparable treatment without inhibitor only 20% of the total plant available N was present as NH_4. The response of the crop as regards yield and N-contents of the grain, however, was nil.

The soils used by Kapusta and Varsa [99] are so called "claypan" soils (Illinois, USA) and are known for losses of N by denitrification, leaching being of minor importance. In the first year of a 2 year experimental period, nitrapyrin at 1.3-2.6 l ha^{-1} and with anhydrous ammonia at 56-168 kg ha^{-1} gave higher yields than the treatment combinations without nitrapyrin ; in the second year with drier conditions, no effects were found.

Townsend and McRae [257] concluded from their work in Nova Scotia, Canada in 1976 and 1977 on a light sandy loam, a sandy loam and silty clay wit 1% nitrapyrin (based on the weight of N in the fertilizer) that, except on light sandy soils, no yield advantage is gained by stabilizing nitrogen in the NH_4 form. At the time of tasseling the contents of NH_4-N were higher when nitrapyrin was banded at 5 cm depth with the fertilizer (a 10-10-10 composition) but in this treatment as well as in the treatment without stabilizers the amount of NO_3-N was sufficient to cover the need of the crop.

An indirect effect of a NH_4-N stabilizer (in this case nitrapyrin) was discussed by Tsai et al. [261] from their findings that a greater amount of sucrose (measured by ^{14}C) was translocated from leaves to grain under NN_4^+ rich conditions. Thus the grain yield of maize was found to be higher in the treatments with nitrapyrin.

Another indirect effect of nitrification inhibition via compounds such as nitrapyrin is to increase crop yield by reduction of plant diseases. This aspect will be discussed in 7.2. In experiments on this subject with maize as a test crop, White et al. [282] found no consistent results on "stalk rot" and no differences in yield. The results of Warren et al. [274] are more positive with a reduction of "stalk rot" incidence and increased yield of maize when nitrogen was kept as NH_4 for a longer period by using nitrapyrin as an inhibitor of nitrification.

Dibb and Welch [52] studied the effect of NH_4 versus NO_3 absorption on yield and chemical composition of maize in greenhouse pot culture. NH_4-N was prevented from nitrification with nitrapyrin applied at amounts up to 100 mg per kg soil. Yield reduction was found when, with NH_4-N-nutrition, the N : K ratios exceeded 2 : 1.

Since no phytotoxic effects of nitrapyrin as such could be found, an imbalanced cation-anion uptake, especially for potassium and not of NH_4 per se is given as an explanation. The authors emphasize the short growth period of the crop in these pot cultures and suggest doing tests in the field as there the conditions, i.e. ratios of N : K, are less extreme.

Nair and Sharma [161] and Kethar [101], mentioned by Prasad [187], tested maize with $(NH_4)_2SO_4$ (N:75-150 kg ha^{-1}) and "neem cake" (4.5.1) and found a positive effect on yield in India both in experiments and on farmers fields.

Some research on maize with N-dressings and N-stabilizers in the USSR is summarized by Smirnov [234] and Tetruashvili et al. [247]. The field and pot experiments they mention show a positive effect of N-Serve and AM. Pot experiments with barley, maize and vetch and N-Serve showed [15] a small dry matter yield reduction for 7 week old maize. The authors used a calcareous soil (pH 8.2) and relatively large amount of NH_4-N (as NH_4NO_3). These conditions may be toxic especiallu for *Nitrobacter* spp (3.2.2).

5.3 Potatoes

Two main conclusions can be drawn from work with potatoes and nitrification inhibitors viz. potatoes are more susceptible to NH_4-N than other crops (for instance cereals (5.1 and 5.2)) and NH_4-N reduces the incidence of diseases such as potato (common) scab (*Streptomyces scabies*) and "wilting" caused by *Verticillium* sp.

The effect of NH_4-N was studied by Polizotto et al. [183]. Growth was reduced severely, in water cultures with only NH_4-N in the solution irrespective of the pH of the solution, and uptake of Ca and Mg were reduced whereas P and N were taken up in greater amounts than with plants with NO_3-N.

In field experiments with potatoes Hendrickson et al. [74] found a yield reduction and decreased quality of tubers with up to 4.4 kg ha^{-1} nitrapyrin in combination with $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ at amounts of 270 kg ha^{-1} N. With these relatively high rates of N and NH_4-N available in the light textured soil for a prolonged period such results can be expected.

Potter et al. [184] found no differences in yield when applying ammonium sulphate with and without N-Serve on Michigan sandy loam soils, which are low in available nitrates, whereas the yield and number of marketable tubers increased on Idaho soils with the same fertilizers and N-Serve at 1.12 kg ha^{-1}. According to Roberts [201] no effects of the inhibitors nitrapyrin and terrazole both at 0.56 kg ha^{-1} were found with band-(row)application of nitrogen as urea, at 224 kg ha^{-1}N. Broadcast application of N, as urea, with spraying of the inhibitor followed by thoroughly mixing the compounds with the soil, gave some yield increases for both inhibitors on Washington soils.

"Neem cake" at rates of 10% of the urea dressing increased potato yields (Kethar [101] cited by Prasad [187]) but with levels of 20% of the inhibitor there were yield reductions.

5.4 Grassland

Thorough mixing of soil and fertilizer, with other compounds as nitrification inhibitors, is impossible on grassland under natural conditions. Fertilizers etc. must be applied broadcast or by injection.

Results of work in Great Britain [12,12] are summarised in Table 5.3. NH_3 was injected in autumn (November) or spring (March) at 375 kg ha^{-1} N at 30 or 60 cm intervals.

CS_2 (Carbon di sulphide, described in 4.6) was also used and was a more efficient nitrification inhibitor since the compound diffuses from the point of injection. The authors conclude that under conditions of a mild and rainy winter, with leaching, inhibitors increase the efficiency of ammonium-and or urea-nitrogen applied in autumn.

From their work in New Zealand, Turner and McGregor [264] concluded that nitrapyrin is of no practical use on pastures. Broadcast application of urea coated with terrazole (described in chapter 4.3) in amounts as N, of upto 400 kg ha^{-1} gave no more yield than untreated fertilizer whether applied in spring or autumn. The effects of retarded nitrification were expressed in NH_4-N and NO_3-N contents of soil samples but also in lower nitrate contents of grass (*Lolium-perenne*,L) shortly after application of the inhibitor. As New Zealand pastures mostly consist of grass-clover mixtures, more or less an ecological climax vegetation [138], nitrogen is symbiotically fixed in an ammonical form in the nodulated roots of the clover plants. For this reason extra NH_4-N is apparantly not needed while according to these authors, soil pH in most pastures is below 6 so that nitrification will not be optimal.

Poletschny and Sommer [182] studied the effects of nitrapyrin in combination with ammonium sulphate, urea and calciumcyanamid; also calcium-nitrate and ammonium nitrate limestone and a DCD-urea fertilizer (= urea + DCD, see chapter 4.1) in their 3 years experiments on a sand, a loam and a clay soil. They used *Lolium perenne* L. as a test crop and so-called field isolated plots (frame beds) of 2 m^2 with nitrogen applied at up to 200 kg ha^{-1}.

NH_4-N increased yield and N-uptake in the first cut, but NO_3-nutrition was found to give the highest total yield and N-uptake for three cuts of grass.

Table 5.3 Effect of nitrogen and nitrification inhibitors (sodium trithiocarbonate)(STC, see 4.6) and nitrapyrin) on dry matter yields of grass and nitrogen uptake after three cuts at Rothamsted and Woburn. From J Ashworth, FV Widdowson, A Penny, E Bird, MV Hewitt and EJ Gibbs [12]

Item	Nil N	NH_3 (Nov)	NH_3 (March)	NH_3+STC (March)	NH_3+NServe (March)	Nitrochalk
Rothamsted						
Yield (ton ha^{-1})	6.0	11.6	11.1	11.5	11.8	12.4
N harvested (kg ha^{-1})	90	288	278	291	294	306
Woburn						
Yield (ton ha^{-1})	1.0	8.6	6.9	5.4	5.8	11.0
N harvested (kg ha^{-1})	13	192	142	114	126	221

Nitrochalk = Calcium Ammonium Nitrate

Addition of nitrapyrin (N-Serve) to ammonium fertilizers or urea increased total N uptake. The DCD-urea proved to be inferior to the other nitrogen forms, especially at the germination stage of the crops.

In a lysimeter experiment with peat soils of different pH and with addition of nitrapyrin at 10 mg kg^{-1} and DCD at 60 mg kg^{-1} to the (20 cm) surface layer of the soil, Scheffer [223] found no effect on yield and nitrate contents of *Lolium perenne*, L. This is reasonable as high NO_3 contents were found in the soil even without N-dressing.

With Italian rye grass Nowakowski [170] found lower NO_3 contents shortly after dressing or re-dressing with ammonium sulphate (N:224 kg ha^{-1}) + nitrapyrin at 2% of the weight of N. With a dressing of 112 kg ha^{-1} no differences were found between ammonium sulphate (with or without inhibition) and sodium nitrate. In a pot experiment with ryegrass and forced leaching (by percolation) application of DCD with cattle liquid manure increased yield and N uptake [6].

The manure was mixed with part of the soil in the pots 4,2,1 and 0 weeks before seeding and thus incubated under aerobic conditions. Also in pot experiments with cocksfoot (*Dactylis glomerata*,L.) Chodan and Kucharshi [417] found no remarkable effects of N-Serve at rates of 0-20% of the fertilizer-N in combination with ammonium sulphate and urea. A somewhat higher yield and N-uptake for individual cuts as well as for total yield of grass from five cuts was found with 2.5% N-Serve.

The NO_3-N concentrations in the aerial parts of the test crop were decreased substantially, related to the dose of N-Serve used, from 3407 to 915 with ammonium sulphate and from 3368 to 2447 mg kg^{-1} DM with urea for treatments without and with 2.5% N-Serve respectively.

5.5 Other agricultural crops

Oats was used as a test crop in pot experiments by Jurkowska [95] with nitrapyrin, DCD, thiourea and 0-nitroaniline as nitrification inhibitors. When the compounds were used at 5 mg kg^{-1} soil no yield depression was found, whereas at 25 mg kg^{-1} DCD was the only effective inhibitor not to cause substantial reduction of yield.

Barley and vetch were tested with N-Serve by Aydeniz et al. [15]. These authors used also maize (5.2). N alone increased yield and with N at 50 mg kg^{-1} soil addition of N-Serve (at 7 kg per ha) also had a positive effect. The yield reduction of vetch at N=50 as well as for N=200 mg per pot was supposedly caused by toxic effects on Rhizobium (see 2.4 and also Riley and Barber [200]).

Swezey and Turner [245] and Hagemann and Meyer [69] (cited by Hills, et al. [82]) used nitrapyrin in their studies with sugar beet. The former observed a 10% yield increase with nitrapyrin, at 0.5% of the N applied, mixed with ammonium sulphate or applied wirh anhydrous ammonia and side dressed. Hills et al. [82] found more roots and tops but a lower sucrose content and thus no differences in sucrose and dry matter yield when they applied N-labelled ammonium sulphate as a side-dressing.

Urea, urea-ammonium nitrate solution and anhydrous ammonia combined with nitrapyrin and 5-ethoxy-3-(trichloromethyl)-1,2,4-thiadiazole (Dwell or etra-diazole, see chapter 4.3) as inhibitors dit not increase yield nor improve efficiency of N applied to grain sorghum by Westerman et al. [292] during a period of 4 years (1976-1979). Even with supplementary irrigation to promote leaching and/or denitrification no positive effects were found under the climatic conditions that exist in the southwest of the USA.

6 EFFECTS OF INHIBITORS ON HORTICULTURAL CROPS

Many horticultural crops have a short growing season and need much plant nutrient. Hence, they usually benefit from high rates of natural manure or fertilizer and are relatively sensitive to changes in moisture conditions, nutrients and other growth factors.

The principles of using inhibitors are the same as for the agricultural crops (5) A possible extra consequence of maintaining high levels of NH_4 is to lower the nitrate content of leafy crops [238].

A number of factors affect the NO_3 content of vegetables.
Among these light conditions, nitrogen fertilization and variety are most important [48]. It should be emphazised however that a relatively high amount of NH_4-N in the growth medium does not assure yield, as was seen for agricultural crops (chapter 5), nor does it necessarily reduce nitrate content, as was discussed for instance by Breimer [293].

Sommer and Mertz [238] compared some vegetables in a pot experiment with a loess soil (pH 7.1) and nitrogen, at 2 g N per pot, as $Ca(NO_3)_2$ and $(NH_4)_2SO_4$ (table 6.1.) or NH_4-N added with nitrapyrin at 10 mg per kg soil.

The results (some of which presented in table 6.1) give a lower NO_3-N content with substantial yield decreases (except for black radish) differing between crops. The effect of NH_4-N on growth and development of plants explains part of the differences between species [73,18].

The aspect of inhibitors on the chemical composition of plants is discussed by Jurkowska [94], Jurkowska and Wojciehowicz [96] and Jurkowska, et al. [294] and illustrated by results of experiments with increasing doses of dicyandiamid (DCD) combined with urea or NH_4NO_3 on oxalic acid contents and contents of P, K, Ca, Mg and minor elements in spinach and sorrel. The increase of N and P in the treatments with inhibitor as well as those of Cu and Mo and, on the other hand, the decrease of K-, Ca- and Mg- contents are results of the nitrogen form i.e. the NH_4-N. In the following sections the results of research on inhibitors are arranged by crops (= plant species).

6.1 Spinach Spinacia oleracea *L)*

Bengtsson [23] found that spinach yields in a field experiment were reduced by 20% or more by nitrapyrin at 2% of the N applied as ammonium sulphate. Moore [150] and Moore et al. [151] found positive effects on yield in field, greenhouse and growth chamber experiments, with lower nitrate contents and higher P, Fe- and vitamin A-contents with N-Serve as inhibitor. The results of Breimer [294] with N-Serve at 1% of N-applied in field experiments in 1977 and 1978 showed no effects on yield or nitrate contents. It should be mentioned that mixing of the N-Serve with the soil was not sufficiently thorough in the latter experiments and the soil, a river clay loam,

Table 6.1 Yield, NO_3- and total nitrogen contents of some horticultural crops grown in pots with nitrogen as NO_3 or NH_4 (the latter in combination of nitrapyrin). From K Sommer and M Mertz [238]

	Dry matter yield (g per pot)		NO_3-N (% in DM)		N-total (% in DM)	
Crop	NO_3-N	NH_4-N	NO_3-N	NH_4-N	NO_3-N	NH_4-N
Chinese cabbage	23.8	17.8	1.00	0.13	4.83	5.51
Mustard	39.5	19.6	0.13	0.14	2.62	4.51
Black radish	30.6	42.4	0.39	0.11	3.50	3.99
Savoy cabbage	36.8	27.0	0.19	0.12	2.91	3.96
Spinach	10.6	9.0	0.46	0.28	4.69	5.80
Carrots	23.8	13.1	0.39	0.16	3.33	4.78
Lettuce	13.5	7.5	0.41	0.18	3.53	5.10

showed an ammonium fixation capacity that was more pronounced than expected.

Results of greenhouse spinach growing with different amounts of N-Serve in combination with ammonium sulphate and a series of ammonium sulphate + Alzodin (compound mentioned in 4.1.1) combinations (Table 6.2) show no effects of N-Serve at the rates tested (0-20 ml per m^2) on yield and NO_3-contents [209]. Alzodin increased NH_4-N contents of soil samples after cropping, but a yield reduction of around 20% had to be accepted; NO_3 contents decreased by as much as 40%.

Pot experiments [230,141,93,94] have shown lower NO_3 contents without reduction in yield when using Nitrapyrin [150,141], DCD [94] or DCD+Nitrapyrin and others [93] as inhibitors.

On the other hand Merkel [134,135] showed in water culture (ph constant) and varying NO_3:NH_4 ratios in the nitrogen source that yield decreased substantially at 40% NO_3 or less, since assimilation and accumulation of glumatine and asparagine uses up a part of the energy that cannot be used for building up dry matter. Also Mills et al. [139,141] recorded yield reductions with 75 or 100% of the nitrogen as NH_4 and found symptoms of ammonium toxicity in these treatments. The NO_3 contents in spinach proved to be low under such conditions, but the authors als found low contents, irrespective of the NO_3:NH_4 ratios, when the amounts of nitrogen in the pots were at such levels that the plants exhausted all the available nitrogen. This aspect of N uptake from a pot with a limited volume of soil should be taken into account in the interpretation of NO_3-N contents of pot grown plants. Mills et al. [141] tested spinach not only in pots in the open but also in growth chambers. The NO_3-content was 2.03% for N=400 mg per pot in the growth chamber against 1.08% for N=800 mg per pot as KNO_3 in the open because of the relatively low light intensity and a short day length (12 hours) in the growth chambers.

Table 6.2 Yields and NO_3-contents of spinach for the fresh market grown in greenhouses in the spring of 1981 with N-Serve, ammoniumsulphate and Alzodin. From JPNL Roorda van Eysinga and MQ van der Meijs [209].

N-Serve 24E (ml per m^2)	0	2.5	5	10	20
Spinach, yield (kg m^{-2})	2.29	2.49	2.30	2.34	2.50
NO_3 contents (mg kg^{-1} fresh weight)	1273	1319	1264	1236	1291
Ammonium sulphate g m^{-2}	100	75	50	25	0
Alzodin g m^{-2}	0	25	50	75	100
Spinach, yield (kg m^{-2})	2.29	2.06	1.98	1.74	1.79
NO_3-contents (mg kg^{-1} fresh weight)	4277	3808	3234	2791	2480

DCD and nitrapyrin were used in pot experiments [102] at rates of 100 and 10 mg per kg soil with a sandy loam (pH 6.8) and with ammonium sulphate, sodium nitrate and calcium cyanamide as N-carriers. With nitrapyrin and ammonium sulphate the same symptoms were found as in the hydro culture with high rates of NH_4-N [134,135]. With DCD and ammonium sulphate the growth of spinach was not restricted as the nitrification was not completely inhibited. At the final harvest the NO_3-N contents were 1.16 and 0.73% for treatments with sodium nitrate or ammonium sulphate without inhibitor at N=1500 mg per pot. Ammonium sulphate + nitrapyrin or DCD gave 0.11% NO_3-N, whereas the contents with calcium cyanamide were intermediate.

6.2 Lettuce (mostly Lactuca sativa *L.var* capitata, *L)*

In field experiments NH_4-N and nitrapyrin did not affect lettuce yield [150,152]. In some of the experiments, mostly those with frequent irrigations, there was a yield increase. The most pronounced increase was shown by Welch et al. [280] in California, USA on an irrigated loam soil, with ammonium sulphate as a N-carrier and N-Serve at 0.56 kg ha^{-1}. The authors suppose lower leaching N-losses with inhibited nitrification. NO_3-N contents of lettuce grown in the open [150] with N at 168 and 202 kg ha^{-1} averaged 0.81, 0.88 and 1.06% with anhydrous ammonia alone, anhydrous ammonia + N-Serve (at 1 kg ha^{-1}) and ammonium sulphate applied in 3 doses, respectively. The contents are those of oven dry midribs of wrapper leaves sampled 3 weeks prior to harvest. Analysis of edible head tissue sampled at harvest in another experiment by the same author showed 0.36 and 0.31% NO_3-N for ammonium sulphate in three dressings and ammonium sulphate in one application with N-Serve. The reductions proved not to be significant at the 5 percent level of probability. The author mentions a dark green colour of the heads grown with N-stabilizer (as N-Serve is called) and states that no visible or measurable harmful effect of N-Serve was apparant in the plants prior to harvest and also not after 11 days under refrigeration.

Research work with lettuce under glasshouse conditions and with DCD as well as nitrapyrin as inhibitor was carried out by members of the Glasshouse Crops Research and Experiment Station, Netherlands [165,136,206,250,209].

Nederpel, Van der Meys and Roorda van Eysinga [165] tested DCD at 14 and 150 kg ha^{-1} and found no effects on lettuce yields. As the highest doses gave some symptoms described as "leaf burning" these amounts are probably close to the admissible dose. The NO_3-N contents decreased by from 14 to 68% for these amounts of inhibitor; the contents without inhibitor ranging from 1.44 and 2.69%, with soil type and variety [136]. In more recent work [207] with DCD at up to 15 g per m^2 no yield reduction was found but NO_3-N contents decreased from 1.03 to 0.34% on a coarse sand and from 1.34-0.81% on a clay soil with dressings of 100 g per m^2 of ammonium sulphate. Roorda van Eysinga and Janssen [206] tested nitrapyrin and calcium cyanamide on two sandy soils with pH KCl 5.8, organic matter 7.7% and pH KCl 6.3 and organic matter 10.0% respectively. With dressings of 100 g per m^2 of ammonium sulphate and 0,1,2 or 4 cm^3 of nitrapyrin per m^2 and 100 g per m^2 calcium cyanamide no effects on yield were found on the first soil and the reduction of NO_3-contents was slight. On the second soil calcium cyanamide, gave lower NO_3-contents and also lower yields whereas with nitrapyrin there were no such effects.

Tooze et al. [250] tested lettuce under glass in spring on four soil types differing in texture and organic matter content. Doses of nitrapyrin of up to 20 ml per m^2 had no harmful effect on yield and resulted in a substantial decrease in NO_3-contents. The effects of DCD up to 120 kg ha^{-1} were similar to those found by Nederpel and Roorda van Eysinga [165]. In the spring of 1981, Roorda van Eysinga and Van der Meys [209] compared anhydrous ammonia and ammonium sulphate both with N-Serve as inhibitor and tested Alzodin (a fertilizer mentioned in chapter 4.1). Part of the results (comparable with those of spinach in 6.1.) are presented in Table 6.3.

Increasing doses of N-Serve had no effect on yields whereas NO_3-contents decreased by some 10% according to soil type. With Alzodin (= ammonium sulphate + DCD) the effects on yield are negligible, but the NO_3-contents decreased by 72 or 62% for the two soils with Alzodin at 100 g/m^2 compared with ammonium sulphate without DCD at 100 g per m^2.

Table 6.3 Yield and NO_3-content of lettuce grown under glass in spring 1981 with N-Serve, ammonium sulphate and Alzodin on a marine clay soil coded L, a peat marine clay soil (organic matter 33%, particles < 16 µm 47%) coded N and a light textured river clay soil (organic matter 7.5%; particles <16 µm 19%) coded as Pl

N-Serve 24 E (ml per m^2)		0	2.5	5	10	20
Lettuce yield (g per head)	L	169	161	169	166	160
	N	309	309	313	310	309
	Pl	224	220	218	216	206
NO_3-contents	L	2665	2345	2254	2022	1748
(mg kg^{-1} fresh weight)	N	3552	3085	2953	3129	2922
	Pl	1999	2422	2224	2092	1790
Ammonium sulphate g per m^2		100	75	50	25	0
Alzodin g per m^2		0	25	50	75	100
Lettuce yield (g per head)	N	315	-1)	333	-	322
	Pl	250	-	230	-	236
NO_3-contents	N	3222	-	2390	-	2304
(mg kg^{-1} fresh weight)	Pl	3224	-	3145	-	2006

1)-Treatment combination not tested.

*6.3 Radish (*Raphanus sativus *L,var* radicula *Pers)*

In their work with radish in nutrient solution cultures varying in pH and in ammonium nitrogen (from 0-90 mg l^{-1}) Weir et al. [279] found an optimum level of radish growth is not restricted by low concentrations of NH_4-N. On the other hand this crop belongs to a group with high NO_3-contents in the edible part, a thickened hypocotyl. The work in soils under glass [203,204] or in pots [142,17,222] with various N-sources and inhibitors is directed to effects on yield and NO_3-contents.

Roorda van Eysinga and Van der Meys [203] found DCD at 10 g per m^2 more effective in lowering NO_3-contents than nitrapyrin at 2 ml per m^2 with 80 g per m^2 ammonium sulphate in an experiment in autumn. In early spring the effects of DCD in NO_3 contents even at 2.5 g per m^2, were more pronounced with a slight reduction of yield. Optimum plant weights were found with N at 200-400 mg for pots filled with 1 kg of a mixture of sand, loam and peat [142]. In a first experiment nitrapyrin lowered the NO_3 contents; in a second, with NH_4:NO_3 combinations and 400 mg total N per pot plants showed ammonium toxicity in treatments with NH_4-N+ nitrapyrin.

This treatment also reduced yield significantly.

The results of experiments on a sandy soil [222] with nitrapyrin at 10 mg kg^{-1} in combination with nitrogen as NO_3 or NH_4 and with or without correction for soil pH (pH changes as a result of nitrification) showed that pH 4.5 was too low and inhibited nitrification without inhibitor, whereas with pH correction an accumulation of NO_3-N qas noticed with the highest levels of N in the treatments without addition of nitrapyrin. A pot experiment with radish and fertilizers of organic origin as well as inorganic products [17] showed the interaction of nitrapyrin and organic material as mentioned in 3.2.1. At 400 and 800 mg N per kg soil as urea or ammonium sulphate symptoms of reduced growth, necrotic and curling leaves were noticed.

Notton et al. [171] observed a reduction of nitrate reductase activity for radish, as well as for turnip and cauliflower, grown with different amounts of N-Serve in combination with urea and ammonium-N, of 5-40 percent compared to plants with NO_3-N. The experiments were performed in pots with quartz sand in the presence of root debris and acetone to stimulate denitrification.

*6.4 Cucumber (*Cucumis sativus *L)*

Susceptibility of young cucumber plants to NH_4 was shown by Schenk and Wehrmann [224] in their work with nutrient solutions containing 5 mg l^{-1} dicyandiamide to inhibit nitrification. They discussed [225] the possibility that inhibited roots respiration of NH_4-N treated plants might be the cause of lower yields. Besides nitrapyrin, Zawistowska et al. [284] used its metabolite 6-chloropicolinic acid (6-CPA) with young cucumber plants and found restrictions of uptake of NO_3, K and Ca of 24,17 and 25% respectively and 52, 36 and 28% by 6-chloropicolinic acid at concentrations of 5 μM per litre. According to these authors an auxin like effect on membrane permeability explains the results. Also in sand cultures [222] amounts of nitrapyrin and 6-CPA of 10 mg kg^{-1} substratum showed toxixity symptoms for this crop, The lowest NO_3-contents were found with 6-CPA;

*6.5 Tomatoes (*Lycopersicum esculentum *Mill)*

Because of their sensitivity to ammonium Maynard and Barker [124] and Mills and Pokorny [144,145] used tomatoes as a test crop in organic media of pine bark or peat dressed with ammonium- and nitrate-N with and without nitrapyrin. Application of up to 50 mg kg^{-1} of nitrapyrin inhibited denitrification, thus increasing N-efficiency. In earlier work Merkel [134] found that with DCD in a nutrient solution 20% of the NO_3-N could be replaced by NH_3-N without negative effects on yield. In pot experiments with mixtures of peat and soil, with 25% peat, as a growth medium and nitrapyrin at 100 mg per kg soil no reduction in yield of 30 days old tomato plants was found. An interaction between nitrapyrin and the organic matter of the medium is likely to give a lower effectivity of the inhibitor involved. In this and next experiments, effects of nitrapyrin and other inhibitor were tested on plants in their vegetative stage of growth.

In experiments with tomatoes on a peat vermiculite growth medium and NO_3-N as a nitrogen source [181] nitrapyrin caused growth reduction of shoots at a rate of 50 mg l^{-1} in the substratum. The author suggested that nitrapyrin reduced water uptake and NO_3-N assimilation as he found reduced xylem (water) pressure and a decreased total N content as well as an increased shoot NO_3-N in the relevant treatment combinations.

6.6 Cabbage

Cabbage, specifically *Brassica oleracea* convar. *capitata* (L) Alef. var *Alba* DC) was used in field experiments for a three year period [68] with different N-sources and N-amounts. Ammonium sulphate, compared to sodium nitrate, increased the incidence of black speck disease and the content of K, Ca and Mg in the plants. Addition of N-Serve with ammonium-N did not inhibit the nitrification in an essential way. The authors suggest that the long growth period of this crop, from June to the end of October, lowers the efficiency of the inhibitor. Probably the relatively high soil temperature in summer also favours the decomposition of nitrapyrin (3.2.4).

Roorda van Eysinga and Van der Meys [205] used nitrapyrin and DCD at 0-20 ml per m^2 and 0-10 g per m^2 respectively with ammonium sulphate, at 100 g per m^2 for Chinese cabbage (*Brassica pekinensis*) (Lour.) Rupr.) in greenhouse culture. The inhibitors had no effects on yield whereas with 20 ml per m^2 of nitrapyrin a reduction of the NO_3 contents of up to 40% was found. The authors suppose that the high amount of available NO_3-N before dressing and the favourable conditions for nitrification in the clay soil (pH KCl 6.9) with an organic matter content of 7% resulted in these findings.

6.7 Other horticultural crops (sweet corn, endive, potatoes, mustard turnips)

Work with sweet corn [211] showed no specific effects of nitrapyrin for this crop. Yields were not affected in a dry year but were higher under wet conditions with ammonium sulphate both with and without nitrapyrin.

A differential movement of NH_4-N away from the nitrapyrin was suggested as an explanation of the lack of response [212]. Denitrification was inhibited under field conditions with nitrapyrin and sweet corn as a test crop [127].

Endive (*Cichorium endivia* L) was used with nitrapyrin + injected ammonia or ammonium sulphate and with Alzodin by Roorda van Eysinga et al. [208] and Roorda van Eysinga and Van der Meys [209]. In the latter work no effects of nitrapyrin at rates of up to 20 ml N-Serve 24 E per m^2 on yield and nitrate contents were found, whereas with Alzodin compared to the same amounts of N from $(NH_4)_2SO_4$ there was no yield reduction but NO_3-contents were reduced by 24%. With nitrapyrin, AM (4.2) and ST (4.6) at 1,3 and 9% of the amounts of N added mustard growth was substantially inhibited and yield reduced compared to ammonium sulphate without inhibitor [93]. Roberts [201] evaluated N-Serve and Dwell (= Terrazole, 4.3) as nitrification inhibitors on potatoes with a urea dressing as the control treatment. When the nitrogen was broadcast before planting the N stabilizers (-inhibitors) increased yields and especially yields of first quality potatoes. With the nitrogen side-dressed at planting no differences in yield were found.

Turnip (*Brassica rapa*,L) was used by Notton et al. [171] in sand cultures to test nitrapyrin with urea (see 6.3).

7 OTHER EFFECTS AND ASPECTS OF NITRIFICATION INHIBITORS

7.1 Toxicity

a) Phytoxicity

The phytotoxicity of chemicals, soil constituents and compounds as nitrification inhibitors and their derivatives have mostly been tested on seedlings.

Goring [63] suggested maximum nitrapyrin concentrations to avoid risk of growth reduction of 12.5 mg kg^{-1} soil for tomato seedlings, oats, carrots, onions and lettuce; of 25 mg kg^{-1} for cotton, cucumber and wheat and of 50 mg kg^{-1} of soil for maize, peas, sugarbeet, spinach and radish.

On the contrary, amounts of 1 mg kg^{-1} soil were shown to be toxic for lucerne [128], for *Robinia pseudoacacia* [116,199] and for soya bean seedlings

[200]. For ryegrass and clover 5 mg kg^{-1} soil was found [175]. The symptoms and effects in Robinia and soya beans, were described as "auxin like" and these auxins and related compounds affect membrane permeability and ion uptake [284]. These authors showed a reduction of NO_3 uptake and a lethal dose of nitrapyrin with cucumber seedlings in solution cultures at 5.0 x 10^{-6} M and 2,5 x 10^{-5} M respectively. For 6-CPA these values were 2.5 x 10^{-6} and 1.25 x 10^{-5}. At 5 x 10^{-6} both compounds reduced K- and Ca-uptake whereas Cl uptake was enhanced. In earlier work [mentioned in 284] there were no effects of nitrapyrin and 6-CPA on protein synthesis and NRA (nitrate reductase activity) in cucumber leaves.

Dicotyledons proved to be more sensitive to both nitrapyrin and 6-CPA than monocotyledons [60,61]. The toxic amounts of nitrapyrin were for maize seedlings and wheat 50, for sorghum 100 and for rice 20 mg kg^{-1} soil. These amounts were somewhat higher for 6-CPA. On the contrary, the toxic amounts of 6-CPA proved to be somewhat lower than those of nitrapyrin i.e. 5 mg kg^{-1} soil for tomatoes, cotton, lucerne and soya beans and 10 mg kg^{-1} for sugar beet.

Relatively intensice sorption of nitrapyrin on the organic matter (see 3.2.1) is suggested as an explanation of the different values for the two compounds. 6-CPA and nitrapyrin were shown to be effective, and, under specific conditions, toxic when in contact with the roots of cotton and wheat. There were also toxicity symptoms when nitrapyrin came into contact with the aerial parts [61].

Crops sensitive to low concentrations of NH_4 in particular should be tested for susceptibility to nitrification inhibitor phytotoxicity with NO_3 as nitrogen source. Under these conditions Mills et al. [139,140] found no toxic effects of nitrapyrin with 1 to 100 mg kg^{-1} soil for spinach whereas for a number of other vegetables 50 mg kg^{-1} soil was given as an acceptable level [140].

Nitrapyrin at 10 mg kg^{-1} soil [175] was found to retard ripening of wheat in pots.

Phytoxicity of dicyandiamide (DCD) was tested as early as 1925 [4]. A rate of DCD equivalent to NH_4 at 45 kg ha^{-1} was shown to have no effects or to cause only slight leaf tip burn on wheat in pots, whereas for cow peas 5 kg ha^{-1} was decidedly toxic. The symptoms of leaf tip burning, curling leaves and necrotic spots from the margin to the leaf base were observed in pot cultures with NO_3-N as well as with NH_4-N dressings at DCD-N levels of 16.7 mg kg^{-1} for maize and wheat and at 6.7 mg kg^{-1} for tomatoes and were somewhat similar to those resulting from calcium cyanide used as a herbicide or fungicide. Application of the fertilizer $CaCN_2$ together with DCD to a growing crop therefore should be avoided.

2-5 mg kg^{-1} soil of AM (2-amino-4-chloro-6-methyl-pyrimidine) were not phytotoxic in practice. Growth reductions were found at 10-30 mg kg^{-1}, the most sensitive crops being tomatoes, cucumbers and chinese cabbage [258].

Reduction of dry matter related to stunted stem growth was observed with high doses (20% based on the amount of N) of ST (2-sulfanil-amido-thiazole, see 4.6) [221] and DCS (N-2,5-dichloro-phenyl-succinamic acid, see 4.4) with leguminous plants, more particularly kidney beans.

Comparing nitrapyrin and ATC (4-amino-1,2,4-triazole) on several leguminous plants in pots with one kg of a silty clay loam and in a range of 0-20 mg kg^{-1} of the compounds mentioned nitrapyrin appeared to be the best inhibitor. Phytotoxicity symptoms of nitrapyrin appeared as leaf chlorosis in cowpeas (*Vigna sinensis* L), interveinal chlorosis in chickpeas (*Cicer arictinum* L), and leafcurl in green beans (*Phaseolis vulgaris* L) and green peas (*Pisum sativum* L). ATC produced no symptoms in the latter crops but caused leaf chlorosis in the former three species [117].

b) Mamalian toxicity

This has been tested with laboratory animals. As mentioned before [196,197] 6-chloropicolinic acid(6-CPA) is, in so far we know, the only derivate of nitrapyrin. Nitrapyrin has an acute oral LD 50 for male rats of 1072 mg kg^{-1} body weight, for female rats of 1231 mg kg^{-1}; this characteristic for 6-CPA is 2830 and 2180 mg kg^{-1} respectively [156,157].

7.2 Residual effects and residues in crops

As was seen before [197] nitrapyrin is taken up by plants and is decomposed in soils to 6-chloro-picolinic acid (6-CPA). From this compound, in which the Cl atom was labelled as ^{36}Cl, degradation products as: 2-chloropyridine, inorganic chloride, lipoid compounds and an amide of 6-CPA and a protein, were found in maize and tomatoes [197,131]. Residues of 6-CPA as such were found in a number of crops [97,131,156,197] ranging from less than 0.05 mg kg^{-1} DM to 0.45 mg kg^{-1} DM in red beet roots (Table 7.1) and 0.64 mg kg^{-1} in potatoes. With red beet grown on nitrapyrin treated field dressed with urea Kallio et al. [97] showed that the biological half life of nitrapyrin in beet was only 3 weeks; in the soil more than 4 months (see Table 7.1).

Terrazole (4.3) and a derivative with a carboxy-group instead of the trichloro-methyl was tested on maize dressed with urea-N at 134 kg ha^{-1} and 0.5% of the N as terrazole [174]. The derivative was not found in the grain and other aerial parts of the crops; terrazole contents were 0.006 and 0.022 mg kg^{-1} DM respectively.

7.3 Effects on plant diseases

Effects of nitrification inhibitors on disease are mentioned in 5.1 and 5.3 for wheat and potatoes, respectively. It is evident that retaining N in the NH_4-form can markedly effect the severity of at least three root diseases of

Table 7 Nitrapyrin residues in soil and in red beet roots during the growing season 1977 (Nitrapyrin incorporated with urea on June 8, 1977) From H Kallio, RR Linko, E Tikanmäki and J Puntari [97]

	Nitrapyrin	Nitrapyrin			Nitrapyrin		
	(kg ha^{-1})	(mg kg^{-1}DM)	SE	n1)	(mg kg^{-1}DM)	SE	n
		July 1, 1977			Oct. 1, 1977		
Soil	0	-	-	32	0.02	0.01	16
	2	0.81	0.09	32	0.52	0.05	16
	6	0.95	0.20	32	2.28	0.32	16
	18	7.44	1.31	32	4.61	0.47	16
	34	12.58	1.87	32	9.49	1.50	16
		August 15, 1977			October 1, 1977		
Red beet root	0	-	-	24	<0.00	-	16
	2	0.07	0.016	24	<0.00	-	16
	6	0.19	0.024	24	0.06	0.014	16
	18	0.73	0.123	24	0.33	0.046	16
	34	1.19	0.154	24	0.45	0.056	16

1) N = number of samples; SE = standard error

wheat, viz. *Cercosporella* (eyespot) *Gaeumarromyces graminis* (take all) and *Fusarium* foot rot [178].

The incidences of the first two mentioned are reduced by applying nitrapyrin in combination with NH_4-N under irrigated conditions [86,87]. Whether the positive effect may be related to N-induced changes in rhizosphere pH is not quite clear, though pathogen growth is profoundly affected by pH differences. On the other hand, *Fusarium* footrot might be increased by overfertilization as might be caused by increased N-supply due to prevented nitrification and, thus, reduced leaching and/or denitrification [178].

Stalk rot incidence of different origin was reduced in maize by application of nitrapyrin with NH_4-N [274] and as more ammonium was present in the soil it is suggested that the results stem from altered N-metabolism in plants grown with NH_4-N in contrast to normal nitrate nutrition. The positive effect of nitrapyrin was more pronounced with stalk rot form natural infection than from inoculation [282]. According to White et al. [282] stalk rot from *Colletotrichum grami nicola* was not decreased by nitrapyrin application with nitrogen at 67 kg ha^{-1}, whereas a reduction in disease incidence dit not increase yield or stalk diameter. The authors suggest that the continuous supply of nitrogen throughout the growing season achieved by nitrapyrin explains the positive results.

Potato scab, caused by *Streptomyces scabies*, was markedly reduced in nitrapyrin treatments when the inhibitor was applied at 1.0 - 1.5 kg ha^{-1} with

N as ammonium sulphate and on a soil with a low NO_3-N status [184]. Elemental sulphur was added since it has a mitigating effect on the disease [86].

Terrazole (4.3) is used as a fungicide for control of diseases caused by *Pythium, Fusarium* and *Rhizoctonia* species [168].

8 CONCLUSION FOR AGRICULTURAL AND HORTICULTURE USE OF NITRIFICATION INHIBITORS

The agricultural or horticultural usefulness of nitrification inhibitors can be gauged by whether they improve yield and/or quality of produce. In this respect quality refers to such things as colour, taste and chemical composition.

It is not possible to draw from the literature unambiguous conclusions about the use of nitrification inhibitors as regards yield and quality. This is because of the diversity of soil types and soil conditions, the variation of cultural practices and of plant species that have been used in the research work reported on [34]. According to several authors, the efficiency of nitrification inhibitors is markedly enhanced on light textured soil as such soils are often subject to leaching of NO_3-N [234,253,254,255] whereas in heavy textured soils the compounds used might be adsorbed or absorbed on or in soil components [120]. From the agricultural viewpoint there may be some advantage in maintaining mineral-N in the soil as NH_4 because both nitrate and nitrite are susceptible to loss by leaching and denitrification [58]. These aspects are emphasized by several authors [29,93,141,142,169] for well known inhibitors such as nitrapyrin and dicyandiamide (DCD) as well as for a multitude of pesticides, natural products and artificial compounds mentioned as nitrification inhibitors.

Chemical properties of the compounds used call for special cultural practices, since nitrapyrin, for example, should be worked into the soil and come in close contact with the fertilizer and a relatively large amount of the soil to prevent volatilization [239]. DCD-containing fertilizers can be broadcast, but the contact of the inhibitor with NH_4-N already present will be limited to the surface layers of the soil.

Soil conditions such as texture, organic matter content, pH and temperature and interactions between these have effects on the compounds used as inhibitors as such, but also determine the conditions for nitrification. Higher temperature increases the decomposition of nitrapyrin [80] and DCD [267,269]. The derivative of nitrapyrin, 6-chloropicolinic acid also acts as an inhibitor. Rainfall and to a greater extent the relation between precipitation and transpiration partly determine the efficiency of inhibitors as the aim is to reduce leaching of NO_3-N. In this respect the results of research work in the United States as summarized by Stelly [295] clearly show positive results of nitrapyrin when winter rainfall or rain at the beginning of the growth period give rise to leaching [26,27]. On the contrary, spring precipation in the so called Great Plains is insufficient to leach nitrogen below the rooting zone and thus, yields of maize wheat and other crops were unaffected whether nitrogen was kept as NH_4 by an inhibitor or not [78,79].

The possibility of lowering NO_3-contents in plants by using nitrification inhibitors is discussed especially for horticultural crops [17,25,141,142]. Its is unreasonable to expect too much from these compounds, since the processes of uptake and assimilation of NO_3- and or NH_4-N cannot be regulated for the greatly varying plant species by adding a single compound to the soil. A number of arable plant species prefer nitrogen as NO_3 [133]. Keeping a tolerable NH_4-N concentration in different soil types corresponding to the plant needs for nitrogen during a growth period cannot be easily achieved.

The efficiency of inhibitors measured in pot experiments is generally higher than in field or other outdoor experiments [65]. The compounds can be thoroughly mixed in pots? both leaching and volatilization of plant nutrients and/or inhibitors can be prevented.

Page [176], Burns [36] and other authors drew attention to the different conclusions found in soil samples of incubation experiments if only NO_3- or NH_4-N and not both components are measured, for part of the nitrogen can, under several conditions, be volatilized or immobilized.

Of the number of inhibitors mentioned in the literature over a period of over twenty years [189] only N-Serve, DCD and, to a lesser extent AM have been tested thoroughly. Natural products such as Neem, Karanjin etc. (4.5) have a restricted value in the areas where they are available at low cost.

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References

1. Acevedo A and Pereira JF (1964) Hidrólisis de la urea y del biuret en algunos suelos de Costa Rica. Turrialba 14, 173–177
2. Agoola AA (1978) Influence of soil organic matter on cow pea response to nitrogen fertilizer. Argon J 70, 25–28
3. Alexander M (1961) Introduction to soil microbiology. New York, London: J Wiley and Sons Inc
4. Allison FE, Skinner JJ and Reid FR (1925) Toxicity studies with dicyanodiamide on plants. J Agric Res 30, 419–429
5. Amberger A und Gutser R (1978) Umsatz und Wirkung von Harnstoff-dicyandiamid sowie Ammonsulfat-dicyandiamid-Produkten zu Weidelgras und Reis. Zietschr f Pflanzenernährung u Bodenk 141, 553–566
6. Amberger A und Gutser R (1979) Zur Wirkung von Rindergülle mit Dicyandiamidzusatz zu Weidelgras. Zeitschr f Acker- u Pflanzenbau 148, 198–204
7. Amberger A und Vilsmeier K (1978) Anorganisch katalytische Umsetzungen von Cyanamid und dessen Metaboliten in Quarzsand. I. Mechanismus des Cyanamidabbaues unter dem Einfluss von Eisenoxiden und Feuchtigkeit. Zeitschr f Pflanzenernährung u Bodenk 141, 665–667
8. Amberger A und Vilsmeier K (1979a) Dicyandiamidabbau in Quarzsand und Böden. Zeitschr f Pflanzenernährung u Bodenk 142, 778–785
9. Amberger A und Vilsmeier K (1979b) Umsetzungen von Kalkstickstoff in Quarzsand und verschiedene Böden. Zeitschr f Acker- u Pflanzenbau 148, 1–12
10. Amberger A und Vilsmeier K (1979c) Hemmung der Nitrifikation des Güllestickstoffs durch Dicyandiamid. Zeitschr f Acker- und Pflanzenbau 148, 239–246
11. Ashworth J, Briggs GG, Evans AA and Matual J (1977) Inhibition of nitrification by nitrapyrin, carbondisulphide and trithiocarbonate. J Sci Food Agric 28, 673–683
12. Ashworth J, Widdowson FV, Penny A, Bird E, Hewitt MV and Gibbs AJ (1978) Nitrification inhibitors for grass. Report for 1977, part 1, 276–278, Rothamsted Experimental Station
13. Ashworth J and Rodgers GA (1980) The compatibility of the nitrification inhibitor dicyandiamide with injected anhydrous ammonia. Canad J of Soil Sci 61, 461–463
14. Ashworth J, Akerboom HM and Crépin JM (1980) Inhibition by Xanthates of nitrification and urea hydrolysis in soil. J Soil Sci Soc of Am 44, 1247–1249
15. Aydeniz A, Hatipoglu F and Aktas M (1976) The effect of 'N Serve' on the health of barley, maize and vetch. Proc of the 12th Coll of the International Potash Institute, Bern, Switzerland, Fertilizer use and plant health held at Izmir, Turkey
16. Bains SN, Prasad R and Bhatia PC (1971) Use of indigenous materials to enhance the efficiency of fertilizer nitrogen for rice. Fert News 16, 30–32
17. Baker AV (1977) Growth of radishes on organic or chemical fertilizers in soil amended with nitrapyrin. Hort Sci 12, 417
18. Barker V and Mills HA (1980) Ammonium and nitrate nutrition of horticultural crops. Hort Reviews 2, 295–423
19. Basaraba J (1964) Effect of vegetable tannins on nitrification in soils. Plant and Soil 21, 8–16
20. Beck Th (1977) Verlauf und Steuerung der Nitrifikation in Bodenmodellversuchen. Landw Forschung Sonderheft 33, 85–94
21. Beck Th (1979) Die Nitrifikation in Böden (Literature review). Zeitschr f Pflanzenernährung u Bodenk 142, 344–364

22. Belser LW and Mays EL (1980) Specific inhibition of nitrite oxidation by chlorate and its use in assessing nitrification on soils and sediments. Appl and Environ Microbiology March, 505–510
23. Bengtsson BL (1968) Effect of a nitrification inhibitor on yield and nitrate contents of spinach. Zeitschr f Pflanzenernährung u Bodenk 121, 1–4
24. Bhuija ZH and Walker N (1977) Autotrophic nitrifying bacteria in acid tea soils from Bangladesh and Sri Lanka. J Applied Bacteriology 42, 253–257
25. Boon J van der and Niers H (1980) Nitrificatieremmers (literatuurstudie). Nota no 80, Haren (Gr.), Netherlands: Institute for Soil Fertility
26. Boswell FC, Futral JG and Anderson OE (1974) Comparison of fall applied N under formed beds with conventional spring applications for corn production. Agron J 66, 374–377
27. Boswell FC, Nelson LR and Bitzer MJ (1976) Nitrification inhibitor with fall applied versus split nitrogen applications for winter wheat. Agron J 68, 737–740
28. Boswell FC (1977) Seasonal anhydrous ammonia comparison for corn with and without a nitrification inhibitor. Agron J 69, 103–106
29. Bremner JM and Blackmer AM (1978) Nitrous oxide: emission from soils during nitrification of fertilizer nitrogen. Sci 199, 295–296
30. Breteler H and Smit AL (1974) Effect of ammonium nutrition on uptake and metabolism of nitrate in wheat. Neth J of Agric Sci 22, 73–81
31. Briggs GG (1975) The behavior of the nitrification inhibitor 'N-Serve' in broadcast and incorporated applications to soil. J Sci Food and Agric 26. 1083–1092
32. Brioux CH (1910) Annals Sci Agron Serie 3, 241–281. Ref by Prasad et al. (1970)
33. Broadbent FE, Tyler KB and May DM (1980) Tomatoes make efficient use of applied nitrogen. California Agric 34, 24–25
34. Bundy LG and Bremner JM (1973) Inhibition of nitrification in soils. Soil Sci Soc Am Proc 37, 396–398
35. Bundy LG and Bremner JM (1974) Effects of nitrification inhibitors on transformations of urea nitrogen in soils. Soil Biol and Biochem 6, 369–376
36. Burns JG (1977) Nitrate movement in soil and its agricultural significance. Outlook on Agric 9, 144–148
37. Calancea L (1979) The effect of urease and nitrification inhibitors on the amino-acid content of *Lolium multiflorum.* Buletinul Institutului Agronic Cluj-Napoca Agricultura 33, 33–38, Abstr in Soils and Fert 44, 9904
38. Chambers CA, Smith SE, Smith FA, Ramsey MD and Nicholas DJD (1980) Symbiosis of *Trifolium subterraneum* with mycorrhizal fungi and *Rhizobium trifolii* as affected by ammoniumsulphate and nitrification inhibitors. Soil Biol and Biochem 12, 93–100
39. Chancy HF and Kamprath EJ (1980) Relationship between organic matter content and nitrapyrin rate required to inhibit nitrification. Agron Abstr 166
40. Chisso Corporation, Tokyo, Japan (1981) Controlled release urea fertilizers: urea dicyandiamide fertilizer coating. Chem Abstr 95, 17–18
41. Chodán J and Kucharski J (1977) The influence of 2 chloro-6-(trichloromethyl)-pyridine on cocksfoot crop. Polish J of Soil Sci 10, 71–75
42. Chopra RN, Nayar SL and Chopra IC (1956) Glossary of Indian medical plants. New Delhi: Council of scientific and Industrial Research, p. 31. Cited by Mishra et al. (1975)
43. Clark FE and Paul EA (1970) The microflora of grassland. Adv in Agron 22, 375–435
44. Cochran LV, Papendick RJ and Woody MW (1973) Effectiveness of two nitrification inhibitors for anhydrous ammonia under irrigated and dry land conditions. Agron J 65, 649–653
45. Cochran LV, Warner RL and Papendick RJ (1978) Effect of N-depth and applica-

tion rate on yield, protein content and quality of winter wheat. Agron J 70, 964–968

46. Commonwealth Agricultural Bureau (CAB) (1978) Nitrification inhibitors. Annotated Bibliography of the Commonwealth Bureau of Soil, SB 1983
47. Cooper JE (1980) Inhibition of nitrification in soils treated with pig slurry. Bull Environ Contamination Toxicology 25, 176–180
48. Corré WJ and Breimer T (1979) Nitrate and nitrite in vegetables. Literature survey 39, Wageningen, The Netherlands: Centre for Agricultural Publishing and Documentation
49. Cox WR and Reisenauer HM (1973) Growth and ion uptake by wheat supplied with nitrogen as nitrate, or ammonium, or both. Plant and Soil 38, 363–380
50. Cowie GA (1919) Decomposition of cyanamide and dicyandiamide in the soil. J of Agric Sci 9, 113–136
51. Cribbs WH and Mills HA (1979) Influence of nitrapyrin on the evolution of N_2O from an organic medium with and without plants. Commun in Soil Sci and Plant Anal 10, 785–795
52. Dibb DW and Welch LF (1976) Corn growth as affected by ammonium versus nitrate absorbed from soil. Agron J 68, 89–94
53. Dijkshoorn W (1962) Metabolic regulation of the alkaline effect of nitrate utilization in plants. Nature 194, 165–167
54. Dijkshoorn W and Ismunadji M (1972) Nitrogen nutrition of rice plants measured by growth and nutrient content in pot experiments 2. Uptake of ammonium and nitrate from a water logged soil. Neth J of Agric Sci 20, 44–57
55. Drouineau G and Blanc D (1961) Influence of the nitrogen nutrition on the development and on the metabolism of plants. Agrochimica 5, 49–58 (French with summary in English)
56. El Wali AMO, Le Grand F and Gascho GJ (1979) Effect of urea, N-Serve and sulphur coated urea on growth, nutrient uptake, and yield of corn (*Zea mays* L.). Soil Sci Soc of Florida Proc 38, 1–3
57. English JE, Rufner R and Barker AV (1980) Effect of fertilizer, N rate and nitrapyrin on Ca and Mg nutrition of corn (*Zea mays* L.). Commun in Soil Sci and Plant Anal 11, 1005–1007
58. Gasser JKR (1970) Nitrification inhibitors. Their occurrence, production and effects of their use on crop yields and composition. Soils and Fert 33, 547–554
59. Gaur AC and Mathar RS (1979) Effect of straw, 'Neem' cake and farmyard manure on yield and nitrogen uptake by maize crop. Indian J of Agron 24, 449–450
60. Geronimo J, Smith Jr LL, Stockdale GD and Goring CAI (1973) Comparative phytotoxicity of nitrapyrin and its principal metabolite 6-chloropicolinic acid. Agron J 65, 692–693
61. Geronimo J, Smith Jr LL and Stockdale GD (1973) Effect of site of exposure to nitrapyrin and 6-chloropicolinic acid on growth of cotton and wheat seedlings. Agron J 65, 692–693
62. Göhl B (1981) Tropical Feeds – feed information, summaries and nutritive values. FAO Animal Production and Health Series, 12, Rome: FAO
63. Goring CAI (1962a) Control of nitrification by 2-chloro-6-(trichloromethyl)-pyridine. Soil Sci 93, 431–439
64. Goring CAI (1962b) Control of nitrification of ammonium fertilizers and urea by 2-chloro-6-(trichloromethyl)pyridine. Soil Sci 93, 211–218
65. Goring CAI and Scott HH (1976) Control of nitrification by soil fumigants and N-Serve nitrogen stabilizers. Down to Earth 32, 14–17
66. Gray TRG and Williams ST (1971) Soil microorganisms. In: Haywood UH ed. University Reviews in Botany, Edinburgh, Oliver and Boyd
67. Guthrie TF and Bomke AA (1980) Nitrification inhibitors by N-Serve and ATC in

soils with varying texture. J Soil Sci Soc of Am 44, 314–320

68. Gysi Ch und Stoll K (1980) Der Einfluss der Stickstofform (NH_4 oder NO_3) auf das Auftreten von Blattpunktnecrosen bei Lagerkohl. Zeitschr f Pflanzenernährung u Bodenk 143, 14–25
69. Hagemann RW and Meyer RD (1980) Nitrogen stabilizer gives mixed results. California Agric 34, 14–15
70. Harada T, Oshima Y, Nishihara T, et al. (1964) Soil Sci and Plant Nutrition (Tokyo) 11, 39
71. Harrison RP, Severson DA and Crabtree R (1977) Results from fall applied N-Serve nitrogen stabilizers with ammonium nitrogen fertilizers on winter wheat in the North West. Down to Earth 33, 1–5
72. Hauck RD (1972) Synthetic slow release fertilizers and fertilizer amendments. In: Goring CAI and Hamaker JW, eds. Organic chemicals in the soil environment vol 2, 633–690, New York: Marcel Dekker Inc
73. Haynes RJ and Goh KM (1978) Ammonium and nitrate nutrition of plants. Biological Rev 53, 465–510
74. Hendrickson LL, Keeney DR, Walsh LM and Liegel EA (1978a) Evaluation of nitrapyrin as a means of improving nitrogen efficiency in irrigated sands. Agron J 70, 699–704
75. Hendrickson LL, Walsh LM and Keeney DR (1978b) Effectiveness of nitrapyrin in controlling nitrification of fall and spring applied anhydrous ammonia. Agron J 70, 704–708
76. Hendrickson LL and Keeney DR (1979a) Effect of some physical and chemical factors on the rate of hydrolysis of nitrapyrin (N-Serve). Soil Biol and Biochem 11, 47–50
77. Hendrickson LL and Keeney DR (1979b) A bioassay to determine the effect of organic matter and pH on the effectiveness of nitrapyrin (N-Serve) as a nitrification inhibitor. Soil Biol and Biochem 11, 51–55
78. Hergert GW, Frank KD and Rehm GW (1978) Anhydrous ammonia and N-Serve for irrigated corn. Soil Sci Res Rep Univ of Nebraska-Lincoln Agron Dept 1978, 31–34
79. Hergert GW and Wiese RA (1980) Performance of nitrification inhibitors in the Midwest (West). In: Meisinger JJ et al. eds ASA Publication 38, 89–105. Madison Wisconsin 53711, Am Soc of Agron and Soil Sci Soc of Am
80. Herlihy M and Quirke W (1975) The persistence of 2-chloro-6-(trichloromethyl)-pyridine in soil. Commun in Soil Sci and Plant Anal 6, 513–520
81. Hewitt EJ, Hucklesby DP and Notton BA (1976) In: Bonner J and Varner JE eds, Plant Biochemistry, 633–681 New York, Academic Press
82. Hills FJ, Abshabi A, Broadbent FE and Peterson GA (1981) Effect of nitrapyrin on uptake of nitrogen by sugarbeet from labeled ammoniumsulphate. J of the Am Soc of Sugar Beet Technology 21, 150–158
83. Hooper AB and Terry KR (1973) Specific inhibitors of ammonia oxidation in Nitrosomonas. J Bacteriology 115, 480–485
84. Horn RC (1978) New aspects of fertilizer technology in better exploration of plant nutrients. FAO Soils Bull 37, 135–142
85. Huber DM, Murray GA and Crane JM (1969) Inhibition of nitrification as a deterrent to nitrogen losses. Soil Sci Soc Am Proc 33, 975–976
86. Huber DM and Watson RD (1970) Effects of organic amendment on soilborne plant pathogens. Phytopathology 60, 22–26
87. Huber DM and Watson RD (1974) Nitrogen form and plant disease. Annual Rev Phytopathology 12, 139–165. Also in: Down to Earth 27, 14–15 (1972)
88. Hughes TD and Welch LF (1970) 2-chloro-6-(trichloromethyl)pyridine as a nitrification inhibitor for anhydrous ammonia applied in different seasons. Agron J 62, 821–824

89. International Rice Research Institute (IRRI) (1967) Los Banos Philippines Annual Report 1967, 146–147
90. Jacob KD, Allison FE and Braham JM (1924) Chemical and biological studies with cyanamide and some of its transformation products. J Agric Res 28, 37–69
91. Jain JM, Narayasang G, Sarkar MC and Datta M (1980) An evaluation of nitrification retardation property of *Citrullus coldsynthis* cake and its influence on yield and N uptake by wheat. J of the Indian Soc of Soil Sci 28, 480–484
92. Janssen KA (1969) The influence of 2-chloro-6-(trichloromethyl)pyridine with anhydrous ammonia on corn yield, N-uptake and conversion of ammonium to nitrate. MSc-thesis Univ of Nebraska-Lincoln Dept of Agron (Cited by Hergert GW and Wiese RA (1080))
93. Jung J und Dressel J (1978) Umsetzungsvorgänge und Inhibierungsmöglichkeiten bei Boden- und Dünger-stickstoff. Landw Forschung Sonderheft 34, 74–89
94. Jurkowska H (1971) Effect of dicyandiamide on the content of nitrates and oxalic acid in spinach. Agrochimica 15, 445–453
95. Jurkowska H (1974) Investigations into the content of oxalic acid and nitrates in plants. III Comparison of the effect of several nitrification inhibitors on the accumulation of oxalic acid and nitrates in plants. Acta Agraria et Silvestria, Ser Agraria 14, 25–33
96. Jurkowska H and Wojciechowicz T (1974) Investigations on the content of oxalic acid and nitrates in plants. II Effect of dicyandiamide as an inhibitor of nitrification on the accumulation of oxalic acid and nitrates in plants as depending on the nitrogen doses. Acta Agraria et Sylvestria, Ser Agraria 14, 15–24
97. Kallio H, Linko RR, Tikanmäki E and Puntari J (1980) Effect of nitrapyrin on nitrapyrin residues and nitrate content in red beet roots fertilised with urea. J Sci Food Agr 31, 701–708
98. Kamire KK and Sonar KK (1979) Mineralization of urea-N with 'Neem' (*Azadirachta indica*) and Karanj (*Pongamia glabra*, Vent) cakes. J. of Maharashta Agricult Universities 4, 10–12
99. Kapusta G and Varsa EC (1972) Nitrification inhibitors – do they work? Down to Earth 28, 21–33
100. Keeney DR (1980) Factors effecting the persistence and bioactivity of nitrification inhibitors (Literature review) In: Meisinger et al. eds. Nitrification inhibitors – Potentials and limitations ASA Special Publication 38, 33–47. Madison Wisconsin 53711, Am Soc of Agron and Soil Sci of Am
101. Ketkar CM (1976) Final technical report Khadi and Village Industries Commission. Cited by Prasad, 1979
102. Kick H und Massen GG (1973) Der Einfluss von Dicyandiamide und N Serve in Verbindung mit Ammoniumsulfat als N-Dünger auf die Nitrat- und Oxalsäuregehalt von Spinat (*Spinacia oleracea*) Zeitschr f Pflanzenernährung u Bodenk 135, 220–226
103. Krishnapillai S (1979) Inhibition of nitrification by waste tea ('tea fluff'). Plant and Soil 51, 563–569
104. Kurvits A and Kirkby EA (1980) The uptake of nutrients by sunflower plants (*Helianthus annuus*) growing in a continuous flowing culture system supplied with nitrate or ammonium as nitrogen source. Zeitschr f Pflanzenernährung u Bodenk 143, 140–149
105. Laher M and Avnimeleck (1980) Nitrification inhibition in drip irrigation systems. Plant and Soil 55, 35–42
106. Laskowski DA (1972) Influence of the environment on N Serve stability. Abstr Am Soc Agron, 97
107. Laskowski DA and Bidlack (1977) Nitrification recovery after inhibition by nitrapyrin. Down to Earth 33, 12–17

108. Laskowski DA, O'Melia FC, Griffith JD, Regoli AJ, Joungson CR and Goring CAI (1975) Effect of 2-chloro-6-(trichloromethyl)pyridine and its hydrolysis product 6-chloropicolinic acid on soil microorganisms. J of Environm Quality 4, 412–417
109. Laskowski DA, Regoli AJ and Kurihara NH (1974) Aerobic and anaerobic degradation of ^{14}C-labelled N-Serve in soil. Soil Sci Div Agron Abstracts, 129
110. Lees H (1963) Inhibitors of nitrification. In: Hochester RH and Quastel JH eds. Metabolic inhibitors. Comprehensive Treatise vol 2, 615–629, New York Academic Press
111. Lees H and Simpson JR (1957) The biochemistry of the nitrifying organisms 5. Nitrite oxidation by nitrobacter. Biochem J 65, 297–305
112. Lesham Y and Levin J (1978) The effect of growing alfalfa on subsequent cotton plant development and on nitrate formation in peat soil. Plant and Soil 50, 323–328
113. Lewis DC and Stefanson RC (1975) Effect of N-Serve on nitrogen transformations and wheat yields in some Australian soils. Soil Sci 119, 273–279
114. Liang CN and Tabatabai (1978) Effects of trace elements on nitrification in soils. J of Environm Quality 7, 291–293
115. Lycklama JC (1963) The absorption of ammonium and nitrate by perennial rye-grass. Acta Bot Neerlandica 12, 361–423
116. Lynd JQ, Rieck C, Barnes D, Murray D and Santelmann PW (1967) Indicator plant aberrations at threshold soil herbicide levels. Agron J 59, 194–196
117. Maftoun M, Yasrebi J and Darbekeshti M (1981) Comparative phytotoxicity of nitrapyrin and ATC to several leguminous species. Plant and Soil 63, 303–306
118. Mahli SS and Nyborg M (1978) The fate of fall applied N in northern Alberta as measured by the ^{15}N-technique. 11th Int Congr Soil Sci Soc Edmonton, Canada Proc 1, 370
119. Mahli SS and Nyborg M (1979) Nitrate formation during winter from fall applied urea. Soil Biol and Biochem 11, 439–441
120. Malzer GL, Graff TJ and Lensing J (1979) Influence of nitrogen rate, timing of nitrogen application and use of nitrification inhibitors for irrigated spring wheat and corn. Soil Series Rep on field res in soils, 105, 31–39. University of Minnesota. Cited by Hergert and Wiese, 1980
121. Malzer GL (1979) Progress with nitrification inhibitors. Down to Earth 35, 1–3
122. Manickdam TS, Selvasseelan DDA and Krishnamoorthy KK (1976) Nitrification of urea treated with nitrification inhibitors, coated fertilizers and slow acting fertilizers in soil. Fertilizer News 21, 64–65
123. Matzel W, Mouchova H, Apltauer J und Lippold H (1979) Die Wirkung des Nitrifikationhemmers N-Serve bei der Herbstdüngung von Winter-Weizen mit ^{15}N-Ammonsulfat. Archiv f Acker- und Pflanzenbau und Bodenk 23, 421–427
124. Maynard DN and Barker AV (1969) Studies on the tolerance of plants to ammonium. J Am Soc of Hort Sci 94, 235–239
125. McCall PJ and Swann RL (1978) Nitrapyrin volatility from soil. Down to Earth 34, 21–27
126. McClung B and Wolf DC (1980) Nitrification inhibition by nitrapyrin and terrazole in compost amended soils. Agron Abstr 171
127. McElhannon WS and Mills HA (1981) Inhibition of denitrification by nitrapyrin with field grown sweet corn. J Am Soc Hort Sci 106, 673–677
128. McKell CM and Whalley RDB (1964) Compatibility of 2-chloro-6-(trichloromethyl)-pyridine with *Medicago sativa* inoculated with *Rhizobium melioti*. Agron J 56, 26–28
129. McLaren AD and Skujms JJ (1963) Nitrification by *Nitrobacter agilis* on surfaces and in soil with respect to hydrogen ion concentrations. Can J of Microbiol 9, 729–730

130. Meikle RW (1978, 1979) Prediction of ammonium nitrogen fertiliser disappearance from soils in the presence and absence of N Serve nitrogen stabilizers. Down to Earth 34, 6–10 (1978); Soil Sci 127, 202–209 (1979)
131. Meikle RW and Redemann CT (1966) Tracer study of 6-chloropicolinic acid in corn. J Agric Food Chem 14, 159–161
132. Meikle RW, Youngson CR, Hedlund RT, Goring CAI and Addington WW (1976) Measurement and prediction of the disappearance rates from soil of 6-chloropicolinic acid. Arch Environm Contamination Toxicology 5, 105–117
133. Mengel K and Kirkby EA (1978) Principles of plant nutrition. International Potash Institute Berne Switzerland
134. Merkel D (1973) Der Einfluss des NO_3:NH_4-Verhältnis in der Nährlösung auf Ertrag und Gehalte an organischen und anorganischen Ionen in Tomatenpflanzen. Zeitschr f Pflanzenernährung u Bodenk 134, 236–246
135. Merkel D (1975) Oxalatgehalte und Kationen-Anionen-Gleichgewicht von Spinatpflanzen in Abhängigkeit von NO_3:NO_4-Verhältnis in der Nährlösung. Landw Forschung 28, 38–40
136. Meys Q van der en Roorda van Eysinga JPNL (1977) Dicyandiamide toepassing met als doel het nitraatgehalte van in de winter onder glas geteelde sla te verlagen. Rapport 25 Proefstation voor de Groenten- en Fruitteelt onder Glas, Naaldwijk
137. Michael GM, Schumacher H and Marschner H (1965) Uptake of ammonium and nitrate nitrogen from labelled ammoniumnitrate and their distribution in the plant. Zeitschr f Pflanzenernährung, Düngung u Bodenk 110, 225–238 (German with summary in English)
138. Middleton KR and Smith GS (1979) A comparison of ammoniacal and nitrate nutrition of perennial ryegrass through a thermodynamic model. Plant and Soil 53, 487–504
139. Mills HA, Barker AV and Maynard DN (1972) Effects of 2-chloro-6-(trichloromethyl)pyridine on nitrate accumulation in spinach Agron Abstr Annual Meeting, 99
140. Mills HA, Barker AV and Maynard DN (1973) A study of the phytotoxicity of 2-chloro-6-(trichloromethyl)pyridine. Comm in Soil Sci and Plant Anal 4, 487–494
141. Mills HA, Barker AV and Maynard DA (1976a) Effects of nitrapyrin on nitrate accumulation in spinach. J Am Soc Hort Sci 101, 202–204
142. Mills HA, Barker AV and Maynard DA (1976b) Nitrate accumulation in radish as affected by nitrapyrin. Agron J 68, 13–17
143. Mills HA and Cribbs W (1979) Influence of nitrapyrin and 6-chloropicolinic acid on N_2O evolution. Agron Abstr 161
144. Mills HA and Pokorny FA (1978a) The influence of nitrapyrin on nitrogen retention and tomato growth in sand-bark media. J Am Soc Hort Sci 103, 662–664
145. Mills HA and Pokorny FA (1978b) The effectiveness of nitrapyrin in anorganic medium. Down to Earth 34, 26–28
146. Mishra MM, Neelakantan, Naryan KG and Vyas SR (1972) Studies on the decomposition of organic matter in soil. 2 Effects of Sesbania and Bajra stubble plus 'Neem' cake. J of Res Haryana Agric Univ 2, 150–155
147. Mishra MM, Neelakantan S, Khandelwal KC, Bharadwaj SK and Vyas SR (1975) Margosa ('Neem') seed cake as an inhibitor of nitrification. Soil Biol and Biochem 7, 183–184
148. Mishra MM, Flaig W and Sochtig H (1980) The effect of quinoid and phenolic compounds on urease and dehydrogenase activity and nitrification in soil. Plant and Soil 55, 25–33
149. Mitsui S et al. (1964) The effect of pesticides on denitrification in paddy soil. Soil

Sci and Plant Nutrition 10, 15–23

150. Moore FD (1973) N-Serve nutrient stabilizer. A nitrogen management tool for leafy vegetables. Down to Earth 28, 4–7
151. Moore FD, Riggert CE and Holbrook TB (1977) Effect of fertilizer nitrogen nitrification suppression on spinach in alkaline soil. Hort Sci 12, 412
152. Moore FD and Soltanpour PN (1974) Slow release fertilizers and nitrification suppressants as nitrogen management tools for lettuce. Soil Sci Division Agron Abstr 152
153. Moore DRE and Waid JS (1971) Influence of washings of living roots on nitrification. Soil Biol and Biochem 3, 69–83
154. Moraghan JJ and Albus W (1979) Corn grain yields as influenced by anhydrous ammonia and N-Serve. Ann Rep on Res at Oakes N Dakota State Univ, 1978
155. Müller G und Hickisch (1979) Der Einfluss von Ureolyse- und Nitrifikationsinhibitoren auf Bodenmikroorganismen. Arch Acker- u Pflanzenbau u Bodenk 23, 529–546
156. Mullison WR and Laskowski DA (1974) Toxicological and residual effects of nitrapyrin and its metabolite 6-chloropicolinic acid. Agron Abstr Soil Sci Div, 129
157. Mullison WR and Norris MG (1976) A review of the toxicological residual and environmental effects of nitrapyrin and its metabolite 6-chloropicolinic acid. Down to Earth 32, 22–27
158. Munck H (1958) The nitrification of ammonium salts in acid soils. Land Forsch 11, 150–156
159. Murugappan V and Mishra (1979) N-lignin and Margosa ('Neem') seed cake-blended urea as nitrogen source for wheat. Plant and Soil 52, 131–134
160. Muthuswamy P, Raju GSN and Krishnamoorthy (1977) Effect of nitrification inhibitors on the mineralization of urea in soil. Madras Agric J 64, 290–292
161. Nair KPP and Sharma VP (1976) Utility studies on controlled release nitrogen fertilizers and nitrification retarders in maize. Comptes Rendus 4, Coll Int sur le Controle de l'Alimentation des Plantes Cultivées, Cottenie A ed. Vol 2, 531–54
162. Namioka H and Komahi N (1975) Nitrification inhibitor DCS and its application for upland plants. I Effect of N-2,5-dichlorophenylsuccinamic acid (DCS) as a nitrification inhibitor. Abstr of Nippon dozyohiryogaku zasshi, J of the Sci of Soil and Manure 46, 69–75. Also in: Soil Sci and Plant Nutr 21, 415
163. Namioka H and Komaki N (1975) Nitrification and effect of nitrophosphate with DCS. II Nitrification inhibitor DCS and its application for upland plants. Abstr of Nippon dozyohiryogaku zasshi, J of the Sci of Soil and Manure 46, 76–81. Also in: Soil Sci and Plant Nutr 21, 415
164. Namioka H and Ooshio H (1976) Adsorption, movement and hydrolysis of the nitrification inhibitor DCS. III Nitrification inhibitor DCS and its application for upland plants. J of the Sci of Soil and Manure 47, 114–121
165. Nederpel WAC and Roorda van Eysinga JPNL (1976) Het gebruik van dicyaandiamide met het doel het nitraatgehalte van in de winter onder glas geteelde sla te meten. Verslagen Proefstation voor de Groenten en Fruitteelt onder Glas Naaldwijk, The Netherlands, Report 723/3
166. Nelson DW, Sommers, LE, Huber DM and Warren HL (1977) Conserving energy with nitrification inhibitors. In: Agriculture and Energy Lockeretz W ed. 361–376 New York, Academic Press
167. Nelson LR, Boswell FC and Bitzer MJ (1977) Use of a nitrification inhibitor to improve nitrogen efficiency on winter wheat. Georgia Agric Res Bull 18, 22–26
168. Nelson DW and Huber DM (1980) Performance of nitrification in the Midwest (East). In: Meisinger JJ et al. eds. Nitrification inhibitors – Potentials and limitation, Publ Number 38, 75–88, Madison Wisconsin 53711 Am Soc of Agron and Soil Sci Soc of Am

169. Norris MG (1972) N Serve nitrogen stabilizers ... a practical approach to better fertilizer nitrogen management. Down to Earth 28. 5–9

170. Nowakowski TZ (1968) The effect of a nitrification inhibitor on the concentration of nitrate in grain during growth. Plant and Soil 27, 165–168

171. Notton BA, Watson EF and Hewitt EJ (1979) Effects of N-Serve (2-chloro-6-(trichloromethyl)pyridine) formulations on nitrification and on loss of nitrate in sand culture experiments. Plant and Soil 51, 1–12

172. Nyborg M, Mahli SS, Timmermans J and Leitch RH (1977) Losses of crop available nitrogen from soils. Agric and Forestry Bull Univ of Alberta 33, 33–39

173. Olin Corporation (1976a) Dwell^{TM} nitrification inhibitor. Technical Information 4 pp.

174. Olin Corporation (1976b) Research data on Terrazole^{R} performance as a nitrificide. Interoffice memo, Olin Corp, Japan, 6 pp.

175. Osborn CJ (1977) Some effects of the nitrification inhibitor (2-chloro-6-(trichloromethyl)pyridine) on the use of fertilizer nitrogen and the growth of two wheat varieties. Austr J Exp Agric and Animal Husb 17, 645–651

176. Page ER (1975) The location and persistence of ammonia (aqueous, anhydrous, anhydrous + N-Serve) injected into a sandy loam soil as shown by changes in concentration of ammonium and nitrate ions. J of Agric Sci 85, 65–74

177. Papendick RJ and Engibous JC (1980) Performance of nitrification inhibitors in the North-West. In: Meisinger JJ et al. eds. Nitrification inhibitors – potentials and limitations, Publ Number 38, 107–118, Madison Wisconsin 53–711, Am Soc of Agron and Soil Sci Soc of Am

178. Papendick RJ and Cook RJ (1974) Plant water stress and the development of Fusarium foot rot in wheat subjected to different cultural practices. Phytopathology 64, 358–363

179. Parr JF (1974) In: Pesticides in Soil and Water, 315–339, Madison Wisconsin, Soil Sci Soc of Am

180. Patil ND (1972) 'Neem' (*Azadirachta indica* L.) oil as nitrification inhibitor. Fert News 17, 37–38

181. Pill WG (1981) Effect of nitrapyrin and nitrate level on growth, elemental composition and water relations of tomatoes grown in peat-vermiculite. J Am Hort Soc 106, 285–1289

182. Poletschny H and Sommer K (1977) Stickstoffformenversuche unter Anwendung von Nitrificiden bei Grasansaaten. Landw Forschung Sonderheft 33, 41–51

183. Polizotto KR, Wilcox GE and Jones CM (1975) Response of growth and mineral composition of potato to nitrate and ammonium nitrogen. J Am Soc Hort Sci 100, 165–168

184. Potter HS, Norris MG and Lyons CE (1971) Potato scab control studies in Michigan using N-Serve nitrogen stabilizer for nitrification inhibition. Down to Earth 27, 23–24

185. Prasad R and Turkhead BB (1971) Relative efficiency of nitrogen fertilizers for 'Ganga 101' maize (*Zea mays* L.) as influenced by rainfall. Indian J of Agric Sci 41, 485–489

186. Prasad R, Rajak GB and Lakhdive BA (1971) Nitrification retarders and slow release nitrogen fertilizers. Adv in Agron 23, 337–383

187. Prasad R (1979) Increasing fertilizer nitrogen efficiency with slow release fertilizers and nitrification inhibitors. Fert News 4, 25–32

188. Rajale GB and Prasad R (1970) Nitrification/mineralization of urea as affected by nitrification retarders 'N-Serve' and 'AM'. Current Sci 39, 211–212

189. Ranney MW (1978) Nitrification and urease inhibitors. In: Ranney MW ed. Fertilizer additives and soil conditions, 168–169, Park Ridge, New Jersey, Noyes Data Corp

190. Rathsack K (1978) Die nitrificide Wirkung des Dicyandiamids. Landw Forsch 31, 347–358
191. Rao KP and Rains DW (1967) Nitrate absorption by barley. Plant Physiol 57, 55–58
192. Ray CR, Ramakrishna C and Sethunathan N (1980) Nitrification inhibition in a flooded soil by hexachlorocyclohexane (HCH) and carbofuran. Plant and Soil 56, 165–168
193. Reddy GR (1964a) Effect of mixing varying quantities of dicyandiamide with ammonium fertilizers on nitrification of ammonia in soils. Canad J of Soil Sci 44, 254–259
194. Reddy GR (1964b) Effect of varying quantities of dicyandiamide on the utilization of nitrogen by several crops from sodiumnitrate and ammoniumsulphate. J of Agric Sci 62, 35–38
195. Reddy GR and Datta NP (1965) Use of dicyandiamide in nitrogen fertilizers. J Indian Soc of Soil Sci 13, 135–139
196. Reddy RNS and Prasad R (1977) Fertilizer management in rice-wheat rotation, I Nitrogen. Fert News 22, 3–5
197. Redemann CT, Meikle RW and Widofski JG (1964) The loss of 2-chloro-6-(trichloromethyl)pyridine from soil. J Agric and Food Chem 12, 207–209
198. Redemann CT, Martin RT, Wien JD and Widofsky JG (1965) Tracer study of residues from 2-chloro-6-(trichloromethyl)pyridine in plants. J Agric and Food Chem 13, 518–521
199. Rice EL and Pancholy SK (1972) Inhibition of nitrification by climax ecosystems. Am J of Bot 59, 1033–1040
200. Rieck CE and Lynd JQ (1967) Parameters of chlorinated pyridine toxicity to *Robinia pseudoacacia.* Agron J 59, 507–509
201. Riley D and Barber SA (1970) Toxicity of 2-chloro-6-(trichloromethyl)pyridine in soybeans. Agron J 62, 550–551
202. Roberts S (1979) Evaluation of N-Serve and Dwell as nitrification inhibitors on ‘Russet Burbank’ potatoes. Res Rep, Washington State Univ
203. Rodgers GA, Ashworth J and Walker N (1980) Recovery of nitrifier populations from inhibition by Nitrapyrin or CS_2 Zentralblatt für Bacteriologie, Parasitenkunde, Infektionskrankheiten und Hygiene, Abt. II 135, 477–483
204. Roorda van Eysinga JPNL en Meijs MQ van der (1980a) Verslag van een stikstof bemestingsproef met radijs onder glas geteeld. Intern Verslag no. 2, Proefstation voor de Groenten- en Fruitteelt onder Glas te Naaldwijk
205. Roorda van Eysinga JPNL en Meijs MQ van der (1980b) Proef met nitrificatieremmers bij radijs. Voorjaar 1980. Intern Verslag no. 54, Proefstation voor de Groenten- en Fruitteelt onder Glas te Naaldwijk
206. Roorda van Eysinga JPNL en Meijs MQ van der (1980c) A trial with nitrogen fertilizer quantities and nitrification inhibitors with chinese cabbage grown under glass. Intern Verslag no. 47, Proefstation voor Groenten- en Fruitteelt onder Glas te Naaldwijk
207. Roorda van Eysinga JPNL en Janssen GAL (1980) Verslag van een stikstofbemestingsproef met herfstsla in een warenhuis te Helden. Intern Verslag Proefstation voor Groenten- en Fruitteelt onder Glas te Naaldwijk
208. Roorda van Eysinga JPNL(1980) Het nitraat-‘probleem’ en de glasgroenten. Bedrijfsontwikkeling 11, 215–218
209. Roorda van Eysinga JPNL, Maaswinkel RHM, Meijs, MQ van der en Roozenboom P (1980) Een stikstofbemestingsproef met andijvie onder glas met als doel het nitraatgehalte in het gewas te bestuderen. Intern Verslag no. 14, Proefstation voor Groenten- en Fruitteelt onder Glas te Naaldwijk
210. Roorda van Eysinga JPNL en Meijs MQ van der (1981) Proeven met nitrificatie-

remmers bij sla, andijvie en spinazie in het voorjaar 1981. Intern Verslag no. 27, Proefstation voor de Groenten- en Fruitteelt onder Glas te Naaldwijk

211. Rudert BD and Locascio SJ (1977) Movement of soil nitrogen in a Myakka fine sand as influenced by nitrogen source and nitrapyrin in sweet corn. Agron Abstr 161
212. Rudert BD and Locascio SJ (1979a) Growth and tissue composition of sweet corn as affected by nitrogen source, nitrapyrin, and season. J Am Soc of Hort Sci 104, 520–523
213. Rudert BD and Locascio SJ (1979a) Differential mobility of nitrapyrin and ammonium in a sandy soil and its effect on nitrapyrin efficiency. Agron J 71, 487–489
214. Sabey BR (1968) The influence of nitrification supressants on the rate of ammoniumoxidation in midwestern USA field soils. Proc Soil Sci Soc Am 32, 675–679
215. Sahrawat KL, Parmar BS and Mukerjee SK (1974) Note on the nitrification inhibitors in the seeds, bark and leaves of *Pongamia glabra* Vent. Indian J of Agric Sci 44, 415–418
216. Sahrawat KL and Parmar BS (1975) Alcohol extract of 'Neem' (*Azadirachta indica* L.) seed as nitrification inhibitor. J Indian Soc of Soil Sci 23, 131–134
217. Sahrawat KL and Mukerjee SK (1977) Nitrification inhibitors. I Studies with 'Karanjin', a furanol flavonoid from Karanja (*Pongamia glabra* Vent) seeds. Plant and Soil 47, 27–36
218. Sahrawat KL, Mukerjee SK and Gulati KC (1977) Nitrification inhibitors. II Studies with furana compounds. Plant and Soil 47, 687–691
219. Sahrawat KL (1980a) Control of urea hydrolysis and nitrification in soil by chemicals – prospects and problems. Plant and Soil 57, 335–352
220. Sahrawat KL (1980b) On the criteria for comparing the ability of compounds for retardation of nitrification in soil. Plant and Soil 55, 47–490
221. Sahrawat KL (1981) Karanja (*Pongamia glabra* Vent) as source of nitrification inhibitors. Fert News March, 29–33
222. Sampei M and Fukushima M (1973) Injurious effects of nitrification inhibitors on some crops. Study on nitrification inhibitors, Part 2. Bull of the Nat Inst of Agric Sci 24, 53–59
223. Sander DJ and Barker AV (1978) Comparative toxicity of nitrapyrin and 6-chloropicolinic acid to radish and cucumber under different nitrogen nutrition regimes. Agron J 70, 295–298
224. Scheffer B (1977) Zur Frage der Stickstoffumsetzungen in Niedermoorböden. Landw Forschung Sonderheft 33II, 20–28
225. Schenk M and Wehrmann J (1979a) The influence of ammonia in nutrient solution on growth and metabolism of cucumber plants. Plant and Soil 52, 403–414
226. Schenk M and Wehrmann J (1979b) Potassium and phosphate uptake of cucumber plants at different ammonia supply. Plant and Soil 52, 415–426
227. Schuffelen AC, Lehr J and Rosanow M (1952) Technique of pot experiments. Congr of the Int Soil Sci Soc, Transactions, Dublin
228. Shanker H, Ram B and Rathi KS (1976) Effect of 'Neem' cake blended urea on the yield and uptake of nutrients by rice grown under transplanted and direct sown conditions. J Indian Soc of Soil Sci 24, 211–213
229. Shattock GE and Alexander M (1963) A differential inhibitor of nitrifying microorganisms. Proc Soil Sci Soc Am 27, 600–601
230. Singh UV (1966) Studies on better utilization of non edible oil seed cakes: 'Karanj' (*Pongamia glabra*) seed cake. Indian Agric Res Inst New Delhi, India (cited by Sahrawat et al. 1974)
231. Siegel O und Vogt G (1975) Über den Einfluss eines Nitrifikationsinhibitors auf

die Stickstoffverbindungen des Spinats. Landw Forschung 28, 242–248

232. Sinha NP, Singh SN and Jha BK (1979) Effect of blending urea with 'Neem' cake, petroleumether and alcoholextracts of 'Neem' cake on the yield of wheat and nutrient uptake from calcareous soil. Indian J of Agric Sci 49, 273–276
233. SKW (Süddeutsche Kalkstickstoff-Werke) Trostberg München (1979a) Alzodin^R, Rasendünger mit Langzeitwirkung. Merkblatt 1–7
234. SKW (Süddeutsche Kalkstickstoff-Werke) Trostberg München (1979b) Alzon^R, Merkblatt 1–14
235. Smirnov PM (1978) Anwendung von Nitrifikationsinhibitoren zur Senkung der Stickstoffverluste und zur Effektivitätserhöhung der Stickstoffdüngung, Akademie der Landwirtschaftswissenschaften der DDR, Berlin, Tagungsbericht 155, 165–180
236. Smith MS and Weeraratna GS (1975) Influence of some biologically active compounds on microbial activity and on the availability of plant nutrients in soils. II Nitrapyrin, dazomet, 2-chlorobenzamide and tributyl-3-chlorobenzyl ammonium bromide. Pesticide Sci 6, 605–615
237. Sommer K (1970) Beeinflussung der Nitrifikation und des Stickstoffhaushaltes in Böden durch verschiedene Pflanzenschützmittel. Landw Forschung Sonderheft 25, 22–30
238. Sommer K (1972) Nitrificide Teil 1: Wirkung, Bedeutung und Verfahren zur Selektion nitrificider Wirkstoffe. Teil 2: Ammoniumnitrificide amerikanischer und japanischer Herkunft. Landw Forschung 27II, 64–82
239. Sommer K und Mertz M (1974) Wachstum, Ertrag Mineralstoffaufnahme von Pflanzen beeinflusst durch Ammonium oder Nitrat. Landw Forschung 27, 8–30
240. Sommer K und Rossig K (1978) Einfluss der Art der Nitrifikationshemmung auf den Ertrag bei verschiedenartiger N-Düngung und Vorschlag für eine Klassifizierung. Landw Forschung 31, 291–299
241. Sommer K, Mertz M und Rossig K (1976) Stickstoff zu Weizen mit Ammoniumnitrificiden. Mitteilung 2: Proteingehalte, Proteinfraktionen und Backfähigkeit. Landw Forschung 29, 161–169
242. Soriano S and Walker N (1973) The nitrifying bacteria in soils from Rothamsted classical fields and elsewhere. J of Applied Bacteriology 36, 523–529
243. Spratt ED (1973) The effect of ammonium and urea phosphates with and without a nitrification inhibitor on growth and nutrient uptake of wheat. Proc Soil Sci Soc Am 37, 259–263
244. Subbiah S, Kumar RS, Ramanathan KM and Krishnamoorthy (1979) Effect of 'Neem' seed crush blended urea on the yield of finger millet variety CO-7 in two different soils. Madras Agric J 66, 53–55
245. Swezey ANL and Turner GO (1962) Crop experiments on the effect of 2-chloro-6-(trichloromethyl)pyridine for the control of nitrification of ammonium and urea fertilizer. Agron J 54, 532–535
246. Temme J (1946) Over de afbraak van Ca-cyaanamide in de grond. Diss Landbouwhogeschool Wageningen
247. Tetruashvili VG, Joseliani GI, Aladashvili NZ (1980) Effect of the inhibitor N-Serve on yield of maize and fodderbeet. Agrokhimiya 8, 27–29. Summary in Soils and Fert 45, 953 (1981)
248. Tinker PBH (1979) Uptake and consumption of soil nitrogen in relation to agronomic practice. In: Hewitt EJ and Cutting CV eds. Nitrogen assimilation in relation to agronomic practice 101–122. London, New York, Academic Press
249. Todd RL (1974) Nitrification and cation circulation in soil. Soil Sci Div Agron Abstr, 131
250. Tooze SA, Roorda van Eysinga JPNL and Meijs MQ van der (1980) Experiments with nitrification inhibitors and glasshouse lettuce in spring 1980. Verslag Proefstation voor de Groenten- en Fruitteelt onder Glas te Naaldwijk

251. Touchton JT, Hoeft RG and Welch LF (1977) Loss of N-Serve from soil. Agron Abstr, 167
252. Touchton JT, Hoeft RG and Welch LF (1978) Nitrapyrin degradation and movement in soil. Agron J 70, 811–816
253. Touchton JT, Hoeft RG, Welch LF, Mulvaney DL, Oldham MG and Zajicek (1979) N-uptake and corn yield as affected by applications of nitrapyrin with anhydrous ammonia. Agron H 71, 223–242
254. Touchton JT, Hoeft RG, Welch LF and Argyilan WL (1979) Loss of nitrapyrin from soils as affected by pH and temperature. Agron J 71, 865–869
255. Touchton JT, Hoeft RG and Welch LF (1979) Effect of nitrapyrin on nitrification of broadcast-applied urea, plant nutrient concentrations and corn yield. Agron J 71, 787–791
256. Touchton JT and Boswell FC (1980) Performance of nitrification inhibitors in the South East. In: Meisinger JJ et al. eds. Nitrification inhibitors – Potentials and limitations. Publication Number 38, 63–74 Madison Wisconsin 53711, Am Soc of Agron and Soil Sci Soc of Am
257. Townsend LR and McRae KB (1980) The effect of the nitrification inhibitor nitrapyrin on yield and on nitrogen fractions in soil and tissue of corn (*Zea Mays* L.) grown in the Annapolis Valley of Nova Scotia. Canad J of Plant Sci 60, 337–347
258. Toyoda H, Hatakeyama A and Sakurai M (1978) Slow release and modified fertilizers. In: Proc British Sulphur Corp Part 1, 15
259. Toyo Koatsu Industries Inc Tokyo (1965, 1967) Nitrification inhibitor ‘AM’. Techn Bull, 2 (Sept 1965, March 1967)
260. Toyo Koatsu Industries Inc Tokyo (1968) Nitrification inhibitor Toyo Koatsu ‘ST’
261. Tsai CJ, Huber DM and Warren HL (1978) Relationship of the hernel sink for nitrogen to maize productivity. Crop Sci 18, 399–404
262. Tu CM (1973) Effects of Mocap, N-Serve Telon and Vortex at two temperatures on populations and activities of microorganisms in soil. Can J of Plant Sci 53, 401–405
263. Turner GO, Warren LH and Andriessen FG (1962) Effect of 2-chloro-6-trichloromethylpyridine on the nitrification of ammonium fertilizers in field soils. Soil Sci 94, 270–273
264. Turner MA and MacGregor AW (1978) An evaluation of ‘Terrazole’ as a nitrificide for improving the efficiency of use of nitrogenous fertilizers on pasture. New Zealand J of Agric Res 21, 39–45
265. Ulpiani C (1908) Sulla pretesa fermentazione ammonicale della cianamide. Gazzetta Chim Italia 38, 358–417 (Italian without summary in English)
266. Vilsmeier K (1977) Umsetzung von Kalkstickstoff und dessen Metaboliten und Metalloxiden in Quarzsand und Böden. Diss Technische Universität München
267. Vilsmeier K (1980) Dicyandiamidabbau in Boden in Abhängigkeit von der Temperatur. Zeitschr f Pflanzenernährung u Bodenk 143, 113–118
268. Vilsmeier K und Amberger (1978a) Modellversuche zum Umsatz von gemahlenen Kalkstickstoff und Perlkalkstickstoff in Abhängigkeit von Bodenfeuchtigkeit und Applikationsform. Zeitschr f Pflanzenernährung u Boden K 147, 68–77
269. Vilsmeier K und Amberger A (1978b) Anorganisch katalytische Umsetzungen von Cyanamid und dessen Metaboliten in Quarzsand 2. Cyanidabbau unter dem Einfluss von Metaloxiden und Temperatur. Zeitschr f Pflanzenernährung u Bodenk 141, 677–685
270. Vilsmeier K und Amberger A (1980) Umsetzung von Cyanamid, Harnstoff und Ammonsulfat in Abhängigkeit von Temperatur und Bodenfeuchtigkeit. Zeitschr f Pflanzenernährung u Bodenk 143, 47–54

271. Wainwright M (1977) Effects of fungicides on the microbiology and biochemistry of soils. A review. Zeitschr f Pflanzenernährung u Bodenk 140, 587–603
272. Wainwright M (1980) Effects of pesticides and N Serve on the oxidation of elemental S in soil. Plant and Soil 51, 205–213
273. Walker N (1975) Nitrification and nitrifying bacteria. In: Walker N ed. Soil microbiology, a critical review, 133–146, London, UK
274. Warren HL, Huber DM, Nelson DW and Mann OW (1975) Stalk rot incidence and yield of corn as affected by inhibiting nitrification of fall-applied ammonium. Agron J 67, 655–660
275. Warren HL, Huber DM, Tsai CY and Nelson DW)180) Effect of nitrapyrin and N-fertilizer on yield and chemical composition of corn. Agron J 72, 729–732
276. Wasnik HM (1980) Use of 'Neem' cake coated urea on the economy of nitrogen in wheat variety Kalyansona. J of Maharashta Agric Universities 5, 30–32
277. Weber CR (1966) Nodulating and nonnodulating soy beans isolines. II Response to applied nitrogen and modified soil conditions. Agron J 58, 46–49
278. Weir BL, Paulson KN and Lorenz DA (1972) The effect of ammoniacal nitrogen on lettuce (*Lactuca sativa* L.) and radish (*Raphanus sativus* L.) plants. Proc Soil Sci Soc Am 36, 462–465
279. Weir CC (1969) The fate of 2-amino-4-chloro-6-methyl-pyridine (nitrification inhibitor) in soils. Tropical Agric Trinidad 46, 233–237
280. Welch NC, Tyler KB and Ririe D (1979) Nitrogen stabilization in the Pajaro Valley in lettuce, celery and strawberries. California Agric Sept 1979, 12–13
281. Wetselaar R, Passioura JB and Singh BR (1972) Consequences of banding nitrogen fertilizers in soil. I Effects on nitrification. Plant and Soil 36, 159–175
282. White DG, Hoeft RG and Toughton JT (1978) Effect of nitrogen and nitrapyrin on stalk rot, stalk diameter, and yield of corn. Phytopathology 68, 811–814
283. Yearbook Fertilizers of Japan (1970) 333–338, 364–369 (cited by Hauck RD, 1972)
284. Zawistowska T, Barker AV and Glover LJ (1978) Sensitivity of ion accumulation by cucumber seedlings to nitrapyrin and to 6-chloro-picolinic acid. Crop Sci 18, 293–295
285. Morris DR, Boonkerd N and Vasuvat Y (1980) Effects of N-Serve on soya beans and soil nitrogen transformations. Plant and Soil 57, 31–39
286. Belser LW and Schmidt EL (1981) Inhibitory effect of nitrapyrin on three genera of ammonia-oxidizing nitrifiers. Appl and Environm Microbiol 41, 819–821
287. Owens LB (1981) Effects of nitrapyrin on nitrate movement in soil columns. J Environmental Qual 10, 308–310
288. Nommik H (1958) On decomposition of Calcium Cyanamide and Dicyandiamide in the soil. Acta Agriculturae Scandinavica 29, 404–439
289. Görlitz H und Hecht W (1980) Zur Verminderung der Nitrifikation von Güllestickstoff und Verringerung der N-Verlagerung in den Unterboden durch Zusatz von Wirkstoffen. Arch Acker- u Pflanzenbau u Bodenk, Berlin 24, 151–159
290. Misra KC and Chhonkar PK (1978) Possible utilization of 'Neem' cake for inhibiting nitrification in soil. J Indian Soc Soil Sci 26, 90–92
291. Parmar BS, Sahrawat KL and Mukerjee SK (1976) *Pongamia glabra*: constituents and uses. J of Scientific and Industrial Res 35, 608–611
292. Westerman RL, Edlund MG, Minter DK (1981) Nitrapyrin and Etradiazole effects on nitrification and grain sorghum production. Agron J 73, 697–7
293. Breimer T (1982) Environmental factors and cultural measures affecting the nitrate content in spinach. Diss Agric Univ Wageningen. Also published in: Fertilizer Research 3 (1982)
294. Jurkowska H, Wojciechowicz T and Rogoz A (1981) Effect of increasing doses of dicyandiamide as an inhibitor of nitrification on the content of oxalic acid and

some mineral constituents in plants. Agrochimica (Italy) 25, 29–36

295. Stelly M, ed. (1980) Nitrification inhibitors – Potentials and limitations. ASA Special publication number 38. Publ Am Soc of Agron, Soil Sci Soc of Am, Madison, Wisconsin 53711

Additional reference list, compiled after preparation of the manuscript

A 1. Ashworth J, Widdowson FV, Penny A, Gibbs AJ, Hodgkinson RA and Hewitt MV (1982) Results from an experiment on permanent grass evaluating the cumulative effects of aqueous urea, injected alone or with a nitrification inhibitor, with those of 'nitrochalk'. Journal of Agricultural Science 98, 141–154

A 2. Benkenstein H, Pagel H und Krüger W (1982) Zum Einfluss von N-Serve bei Ammoniumsulfat und Harnstoff-Düngung auf Ertrag und Inhaltstoffe von Grünhafer im Gefäszversuch. Arch Acker u Pflanzenbau und Bodenk Berlin 26, 491–499

A 3. Berg P, Klemedtsson L and Rosswall Th (1982) Inhibitory effect of low partial pressures of acetylene on nitrification. Soil Biol Biochem 14, 301–303

A 4. Chancey HF and Kamprath EJ (1982) Effect of nitrapyrin on N response of corn on sandy soils. Agronomy Journal 74, 565–569

A 5. Chen WD and Chu C (1982) Effect of nitrogen fertilizers and nitrapyrin on yield and quality of sweet corn. J of the Agric Assoc of China 117, 25–36 (Chinese with summary in English)

A 6. Evrard TO (1981) Use of selected N-(2,6-dimethylphenyl)-analine methyl ester compounds as ammonium nitrification compounds. Olin Corp USA 5 pp.

A 7. Fachsymposium über den N-Stabilisator SKW-DIDIN für Flüssigmist 22.10.1981 in Augsburg. Bayerisches Landwirtschaftliches Jahrbuch, Sonderdruck Heft 7, 834–896

A 8. Giri T, Saha D and Mukhopadhyay AK (1982) Effect of nitrification inhibitor N-Serve on ammonium ion fixation in soil. Indian Agric 26, 111–114

A 9. Glémas P (1981) Régulateur de nitrification: la nitrapyrine. Cultivar 1981 (sept), 6

A10. Glintić M, Milovac M and Subotić B (1981) The effect of N-Serve on yield and quality of winter wheat and sugar beet. Agrohemija 3/4, 99–107

A11. Golden DC, Sivasubramaniam S, Sandanam S and Wijedasa MA (1981) Inhibitory effects of commercial potassium chloride on the nitrification rates of added ammoniumsulphate in an acid red yellow podzolic soil. Plant and Soil 59, 147–151

A12. Gotz W (1981) Lysimeterversuche mit zwei Böden zur Harnstoffwirkung und Stickstoffbilanz unter dem Einfluss von Dicyandiamid (DCD) als Nitrifikationshemmer. Inaug Diss Hohe Landw Fakultät Rhein Friedr Wilh-Univ, Bonn

A13. Guthrie TF and Bomke AA (1981) Effect of low temperature and nitrification inhibitor on urea hydrolysis. Canadian J of Soil Sci 61, 529–532

A14. Heyland KU und Braun HV (1981) Ueber den Einfluss von DCD-(Dicyandiamid)-Gaben in Kombination mit schwefelsäuren Ammoniak und Gülle auf den Nitratstickstoffgehalt des Bodens sowie die Abreife und den Ertrag von Körnermais. Landw. Forschung 34, 115–125

A15. Hiltbold AE (1981) Nitrogen economy with nitrificationinhibitors? Highlights of Agric Res Alabama Exp Stat 28, 13

A16. Hoffman R und Enzmann J (1982) Aspekte bei der Anwendung von Nitrifikationsinhibitoren unter tropischen Bedingungen. Beiträge trop Landwirtschaftl Veterinärmed 20, 151–166

A17. Huber DM, Warren HL, Nelson DW, Tsai CY, Shaner G (1980) Response of winter wheat to inhibiting nitrification of fall-applied nitrogen. Agron J 72, 632–637

A18. Hughes TD Nitrification inhibitors, leaching, and time of nitrogen application for corn. Univ. of Illinois, PhD thesis 107 pp.

A19. Iwata Y, Dinoff TM, Bailey JB, Voth V and Gunther FA (1981) Analytical method for nitrapyrin and 6-chloropicolinic acid residues in strawberry fruit. Journal of Agricultural and Food Chemistry 229, 235–239

A20. Kallio H and Sandholm J (1982) Distribution of Nitrapyrin [2-chloro-t-(trichloromethyl)-pyridine] and 2 chloro-6-(di-chloromethyl)-pyridine in red beet treated with Nitrapyrin. J Science of Food and Agriculture 33, 451–455

A21. Kowal JJ and Barker AV (1981) Growth and composition of cabbage as effected by nitrogen nutrition. Commun in Soil Sci and Plant Analysis 12, 979–995

A22. Kucharski J (1981a) The effect of N-Serve on the nitrification of ammonia nitrogen in a silty-peat soil. Polish J of Soil Sci 13, 25–29

A23. Kucharski J (1981b) The effect of N-Serve, applied to the soil with ammonium-sulphate and urea on the yield and chemical composition of some plants. II Sorrel Zeszyty Naukowe Akademii Rolniczo-Technicnej Wolsztynie, Rolnictwo 31, 89–101

A24. Lang DJ, Collins M (1981) N_2-fixation as influenced by nitrification inhibitors 73rd Ann Meeting Am Soc of Agronomy: 89, Am Soc of Agron, Madison, Wisconsin

A25. Li LM, Zhang S, Zhou XR and Pan YHV (1981) Effect of 2-chloro-6-(trichloromethyl)pyridine on the nitrification and microbial activity of soil. Acta Pedologica Sinica 18, 58–70 (Chinese with summary in English)

A26. Lohdi MAK (1982) Additional evidence of inhibition of nitrifiers and possible cycling of inhibitors produced by selected plants in a climax community. Bull of the Torrey Botanical Club 109, 119–204

A27. Mahli SS and Nyborg M (1982) An evaluation of carbon disulphide as a sulphur fertilizer and as a nitrification inhibitor. Plant and Soil 65, 203–218

A28. Mathers AC, Stewart BA and Grunes DL (1982) Effect of a nitrification inhibitor on the K, Ca and Mg composition of winter wheat forage. Agron J 74, 569–573

A29. McCormick RA (1981) Nitrification inhibitors: effects on nitrogen loss from soils and corn yield. Purdue Univ West Lafayette USA 168 pp.

A30. Michaud H, Rock H, Seeholzer J (1982) Process for the production of odorless prilled urea-dicyandiamide fertilizers. US patent no 4.309.206: 3 pp.

A31. Neptune AML, Cruz AP, Muraoka T (1980) Nitrate leaking from soil columns in presence of ammonium sulphate $(NH_4)_2SO_4$) and N-Serve 24E (Nitrapyrin). Anales de ESA 'Luiz de Queiroz' 37, 991–1008 (Spanish with summary in English)

A32. Owens LB Effects of nitrapyrin on nitrate movement in soil columns. J Environ Qual 10 (3), 308–310

A33. Peschke H, Krüger W, Sudnitsyn IJ and Jegorov JW (1981) Zur Stickstoffwirkung bei Weidelgras unter Verwendung eines Nitrifikationshemmers sowie bei differenzierter Saugspannung des Bodens. Wiss Zeitschr der Humboldt Universität Math Nat R 30, 195–199

A34. Pill WG, Sparks DL (1982) Effects of nitrapyrin and nitrogen form on tomato growth, water relations, and ion composition. J Am Soc Hort Sci 107, 487–492

A35. Prasad R (1981) Slow release fertilizers and nitrification inhibitors for increasing fertilizer N-efficiency. Indian Farming 31: 17, 19, 21 and 68

A36. Radwan MA and Debell DS (1980) Effects of different sources of fertilizer nitrogen on growth and nutrition of Western hemlock. Res paper Pacific North West Forest and Range Exp Stat PNW no 267

A37. Rieder G and Michaud H (1981) Some aspects of costs versus efficiency in the use of the nitrification inhibitor Didin (= DCD). British Sulphur cooperation's 4th International Conference on Fertilizer Technology paper no 20, London Jan 1981

A38. Rowaished AK (1981) The effect of 'N-Serve' on reducing root-rot disease of wheat seedlings caused by *Fusarium graminearum*. Acta Phytopathologica Acad Scientiarum Hungaricae 16, 15–21

A39. Rodgers A and Ashworth J (1982) Bacteriostatic action of nitrification inhibitors. Canad J of Microbiol 28, 1093–1100

A40. Sahrawat KL (1981a) Evaluation of the nitrification inhibitor (nitrapyrin) application to a soil-water system for conservation of ammonium released under water logged incubation of soils. Communications in Soil Sci and Plant Analysis 67–73

A41. Sahrawat KL (1981b) Comparison of karanjin with other nitrification inhibitors for retardation of nitrification of urea-N in soil. Plant and Soil, 495–498

A42. Scherer HW und Mengel K Einfluss von Stroh und Nitrapyrin auf den verfügbaren Stickstoff im Boden, den Ertrag und den Stickstoffentzug von *Lolium multiflorum* L. Zeitschr f Pflanzenernährung und Bodenk 144, 254–262

A43. Sharma SW, Singh S, Sharma RP, Parashar KS and Prasad R (1981) Studies on nitrogen carry-over effects of urea, sulphur-coated urea, neem cake coated urea and nitrapyrin treated urea applied to plant sugar cane (*Saccharum officinarum*) crop on the succeeding ratoon. Zeitschr f Acker und Pflanzenbau 150, 207–214

A44. Smirnov PM, Bazilevich SD, Obuskovskay LV (1982) Effect of nitrogen fertilizer and N-Serve on the accumulation of nitrates in vegetable crops. Khimiya v seb'skom khozyaistve 2, 16–19. Abstr in Hort Abstr 52, 5405

A45. Smith SE and Kelley BC (1981) Effects of N-Serve on nitrogen fixation in Trifolium and photosynthetic bacterium *Rhodopseudomonas capsulata*. In: Gibson AH and Newton WE eds. Current perspectives in nitrogen fixation. Elsevier/North Holland Biomedical Press Amsterdam

A46. Thomas PA, Park CN, Page JL and Geronimo J (1981) Considering economic as well as statistical significance in evaluating field trial yield results. Down to Earth 37, 17–19

A47. Torres BC and Alvarado BA (1979) N-Serve and ammonium nitrogen fertilization in the cultivation of wheat. Agr Taenica en Mexico 5, 117–131

A48. Varsa EC, Liu SL and Kapusta G (1981) The effect of nitrification inhibitor on wheat yields and soil nitrogen retention. Down to Earth 37, 1–5

A49. Vendrell PF, Hons FM and Bordovsky D (1981) Effects of nitrification inhibition on nitrate leaching losses and yield of Irish potatoes. 73rd Ann Meeting Am Soc of Agronomy 192, Am Soc of Agron, Madison Wisconsin

A50. Weir BL and El-Zik KM (1980) Response of cotton to nitrogen fertilization and nitrification inhibitors. Brow JM ed. Proceedings Beltwide cotton productions Research Conference Jan 1980, 71–72

A51. Welch NC and Quick J (1981) Fertilizing summerplanted strawberries in California's Central Coast. Calif Agriculture 35, 26–27

A52. Werner W und Kanyaruliga (1980) Zur Dynamik des Nitratsstickstoffgehaltes eines Fahlerde – Stau gleys unter dem Einfluss von Harnstoffdüngung, Nitrificidanwendung und Bewässerung. Beiträge trop Landwirtschaft Veterinärmed 18, 351–360