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脲酶/硝化抑制剂减少农田土壤氮素损失的作用特征

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摘 要: 氮肥过量施用加剧了农田土壤氮素损失,如增加NH_3挥发、N_2O排放及硝酸盐淋洗等,这将降低空气和水体质量并对全球气候产生负面影响。脲酶抑制剂和硝化抑制剂可延缓土壤氮素转化,降低土壤活性氮对环境的负面效应,因此在农业生产中被广泛应用,如N-丁基硫代磷酰三胺(NBPT)、3,4-二甲基吡唑磷酸盐(DMPP)和双氰胺(DCD)。本文重点阐述了脲酶抑制剂NBPT和硝化抑制剂DMPP、DCD在农田土壤中的作用机制及其对环境和农学效应的影响,并揭示影响其施用有效性的主要因素。大多数研究结果表明,NBPT与尿素或有机肥配合施用后能够减少土壤NH_3挥发、N_2O排放和NO_3^-淋洗,并提高作物产量、品质及氮肥利用率;与NBPT类似,两种典型硝化抑制剂DCD和DMPP均能降低土壤N_2O排放和NO_3^-淋洗并提高作物产量,但某些环境条件下也会增加土壤NH_3挥发损失。不同农田生态系统中脲酶/硝化抑制剂的作用效果与抑制剂种类、降雨或灌溉量、土壤pH值和黏粒含量等因素有关。在未来的生产实践中,应根据抑制剂在不同土壤环境下的作用特征来更加科学合理地施用抑制剂。

关键词: 硝化抑制剂;脲酶抑制剂;农田土壤;氨挥发;氧化亚氮排放;硝酸盐淋洗;氮肥利用率

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Characteristics of urease/nitrification inhibitors in reducing nitrogen losses in farmland soils

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Abstract: Excessive application of nitrogen fertilizer aggravates nitrogen losses from agricultural soils, with effects such as increasing ammonia(NH_3) volatilization, nitrous oxide(N_2O) emissions, and nitrate(NO_3^-) leaching, which can reduce air and water quality and have a negative impact on global climate. Urease inhibitors and nitrification inhibitors can delay the transformations of soil nitrogen and reduce the negative effects of soil-reactive nitrogen. Both have been widely used in agricultural production, as N-butylthiophosphoryl triamine (NBPT), 3, 4-dimethylpyrazole phosphate (DMPP), and dicyandiamide (DCD). The mechanisms of urease inhibitor (NBPT) and nitrification inhibitors (DMPP, DCD) in agricultural soils and their effects on the environment and agronomy were comprehensively reviewed in this study, revealing the main factors affecting the effectiveness of its application. Many studies have shown that NBPT combined with chemical nitrogen fertilizer and/or organic fertilizer could reduce NH_3 volatilization, N_2O emission, and NO_3^- leaching, as well as improve crop yield and quality and nitrogen-use efficiency. Similarly, as nitrification inhibitors, both DCD and DMPP could reduce soil N_2O emissions and NO_3^- leaching, increase crop yield, and increase soil NH_3 volatilization loss. The inhibition efficacy of urease/

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nitrification inhibitors is related to the type of nitrogen inhibitors, the form and rate of nitrogen fertilizer, whether rainfall or irrigation is employed, and edaphic conditions such as soil pH and clay content. Therefore, the characteristics and effects of urease/nitrification inhibitors should be considered for scientific and practical applications.

Keywords: nitrification inhibitor; urease inhibitor; farmland soils; ammonia volatilization; nitrous oxide emission; nitrate leaching; nitrogen use efficiency

在农业生产过程中，氮肥的必要投入是保证作物产量并满足人口增长需求的关键[1]。然而，农户为了追求农田作物的高产稳产，盲目和过量施用氮肥，导致氮肥利用率降低。据报道，约有50%的肥料氮并未被作物吸收利用，主要以氨（NH_3）挥发、硝化和反硝化作用等过程释放出的各种气体[包括氧化亚氮（N_2O）]以及硝酸盐（NO_3^-）淋洗等形式排放至大气、深层土壤或水体环境中[2]。这不仅增加了农户的经济效益损失，也对大气、水环境以及人类健康构成潜在威胁[3]。例如，NH_3是空气雾霾或灰霾的主要贡献者[4]。与NH_3挥发相比，N_2O排放量较低，但它是破坏大气臭氧层的主要因子，也是重要的温室气体之一[5]。最新研究显示，全球N_2O排放的增长速度快于联合国政府间气候变化专门委员会（IPCC）的预测，这将使全球气候变化风险加剧[6]。此外，NO_3^-由于其本身带负电荷，易于淋洗至地表水和地下水，造成水体富营养化和地下水污染[7]。因此，如何减少氮素损失、提高氮肥利用率并降低氮素损失对环境的负面影响已引起人们广泛关注。

近年来，除与作物生长相匹配的精细施肥和农田管理措施外，脲酶/硝化抑制剂的利用也是有效阻控农田土壤氮素损失的重要手段。脲酶/硝化抑制剂分别通过抑制土壤脲酶和氨氧化微生物的活性来延缓相应的氮素转化过程，因其具有明显提高氮肥利用率并减少氮素损失的作用，越来越受到人们的重视[8]。Zaman等[9]研究表明，脲酶/硝化抑制剂与化肥或有机肥配合施用有利于增加氮肥利用率、提高作物产量，并可降低由大量施用氮肥引发的环境风险[8]。然而，在不同土壤环境条件下，脲酶/硝化抑制剂的有效性差异较大，目前对其在农田土壤中的作用效果和影响因素仍缺乏系统性研究。

因此，本文以典型脲酶抑制剂N-丁基硫代磷酰三胺（NBPT）和硝化抑制剂3,4-二甲基吡唑磷酸盐（DMPP）和双氰胺（DCD）为例，重点阐明相关抑制剂的作用特征及其对土壤NH_3挥发、N_2O排放、NO_3^-淋洗和作物产量的影响效果及影响因素，以期为脲酶/硝化抑制剂在农业中合理应用和推广提供科学的指导。

1 脲酶抑制剂

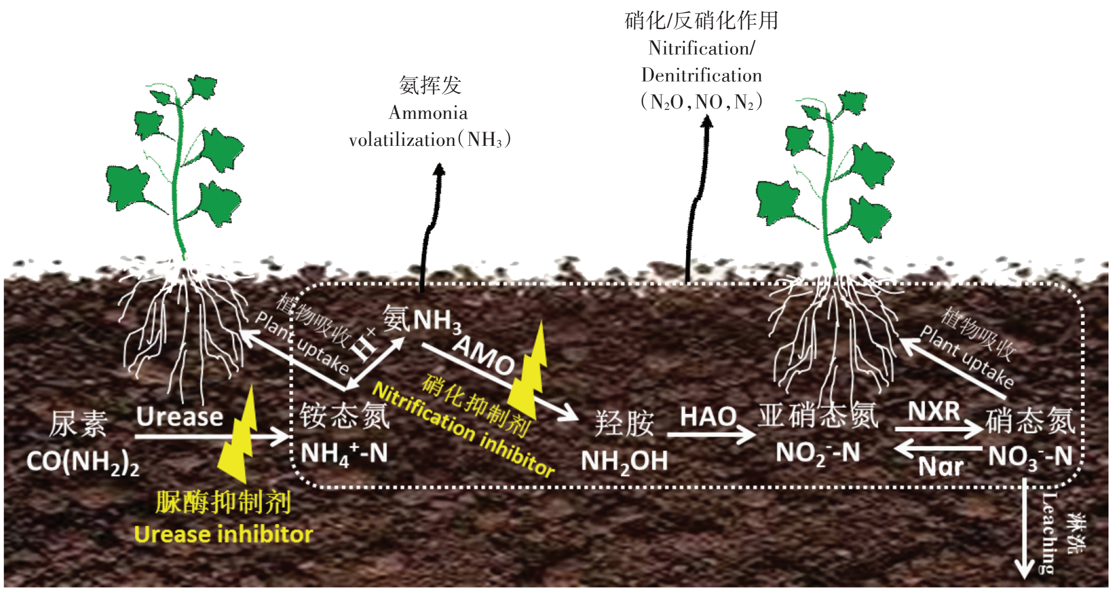
1.1 作用机理

尿素在全球合成氮肥市场中占比约55%，是农业生产上最常用的氮肥类型[10]。尿素施入土壤1~2 d内在土壤脲酶的催化作用下迅速水解为碳酸铵[11]，随后分解为CO_2和铵态氮（NH_4^+-N）[12]。土壤脲酶是一类含镍的金属钛酶，其活性位点包含由氨基甲酸酯桥连在一起的两个镍原子。如图1[13-14]所示，脲酶抑制剂（Urease inhibitor）通过抑制土壤脲酶活性来减缓尿素向NH_4^+-N转化[15]。脲酶抑制剂种类主要包括：①与脲酶巯基基团反应的有机或无机化合物，如氢醌、对苯醌等；②与脲酶活性位点中的镍原子形成络合物的金属螯合物，如乙酰羟肟酸、乙酰氧肟酸；③与脲酶活性位点相结合，不易被脲酶水解的竞争性抑制剂，如NBPT[16]。NBPT是目前研究最多且使用最广泛的脲酶抑制剂[17-18]。NBPT并不直接抑制脲酶活性，而是在有氧条件下先迅速转化为它的氧化产物NBPTo，随后再与脲酶活性位点形成三齿键[19]，进而减缓尿素被脲酶水解的速率[13,20]。由于NBPTo本身降解较快，通常直接使用NBPT更能相对持久地延缓尿素水解[21]。此外，近年来有研究发现，土壤中施入NBPT后氨氧化细菌（AOB）和氨氧化古菌（AOA）的氨单加氧酶基因（*amoA*）拷贝数也显著降低，原因可能是NBPT具有抑制氨氧化菌细胞内脲酶活性的能力，因而减少了胞内硝化作用底物NH_3的有效性，并进一步推测NBPT能够抑制胞内氨氧化菌的硝化作用[22]，但也有研究认为，NBPT对氨氧化菌丰度和种群结构均无影响[23]。

1.2 环境和农学效应

1.2.1 对NH_3挥发的影响

土壤NH_3挥发是农田氮素气态损失的重要途径之一，对大气颗粒物PM_{10}和$PM_{2.5}$的形成具有重要贡献[24]。化学氮肥的施用是农田土壤NH_3挥发最为重要的来源。据报道，施用到土壤表面的尿素中约有25%转化为NH_3并挥发到大气中[25]，而在高温和潮湿的环境条件下，土壤施用尿素后NH_3挥发损失甚至高达40%[26]。



AMO:氨单加氧酶;HAO:羟胺氧化还原酶;NXR:亚硝酸氧化还原酶;Nar:硝酸异化还原酶

AMO:ammonia monooxygenase;HAO:hydroxylamine oxidoreductase;NXR:nitrite oxidoreductase;Nar:membrane-bound nitrate reductase

图1 土壤脲酶/硝化抑制剂的作用机制[13-14]

Figure 1 Inhibitory mechanism of urease and nitrifications in soils[13-14]

脲酶抑制剂与尿素配合施用能够降低土壤NH_3日挥发量,并减少NH_3损失总量[16-17]。Silva等[16]通过大样本分析发现,NH_3在尿素和尿素+NBPT处理中挥发损失比例分别为施氮量的31.0%和14.8%,施用脲酶抑制剂可使氨挥发损失量减少52%。Cantarella等[27]研究发现,与单施尿素处理相比,增施NBPT显著降低土壤NH_3损失量达53%。在稻田土壤中,添加NBPT后NH_3挥发峰值降低27.0%,累积NH_3挥发损失量降低21.7%[28]。室内试验也表明,与单施尿素处理相比,配施NBPT降低了54%~78%的NH_3挥发损失量[29]。脲酶抑制剂还能减缓尿素水解速率,如尿素和尿素+NBPT处理NH_3挥发总量达一半时所用的时间分别为4.8 d和8.3 d[26]。此外,NBPT也可减少有机肥中的NH_3损失。如Li等[30]发现,在有机肥中添加NBPT后,土壤NH_3挥发量由施氮量的15%降为8%。

NBPT抑制土壤NH_3的作用效果受土壤pH、灌溉和降水等因素影响。pH调控土壤溶液中NH_3与NH_4^+的浓度[$NH_4^+(aq) \rightleftarrows H^+(aq)+NH_3(aq) \rightleftarrows NH_3(g)$],是影响土壤$NH_3$挥发的重要因素[31]。在中性或碱性条件(pH>7),易形成NH_3并产生挥发损失,而在酸性条件下,大部分NH_3转化为离子态NH_4^+[32],降低了氨挥发的风险。与低pH土壤相比,在高pH土壤中施用尿素后NH_3挥发潜势较高[33]。Engel等[20]对pH为8.2的沙壤土进行培养(20 ℃)发现,尿素和尿素+NBPT分别在5 d和18 d后完全水解。同时,由于NBPT在酸性土壤中降解快于碱性土壤,因而pH也会影响脲酶抑制剂在土壤中的抑制效果[34]。如在pH 5.6和pH 6.4的土壤中,添加NBPT后NH_3挥发损失比例减少52%~53%,而在pH为4.5的极酸性土壤中,NBPT减少NH_3损失的比例仅为18%[35]。此外,Holcomb等[36]发现在砂质壤土中,增加灌溉量可显著降低NH_3损失。大量降雨或灌溉能够降低土壤NH_3挥发损失,甚至使NBPT无法产生抑制效应。

1.2.2 对温室气体N_2O排放的影响

N_2O作为对流层重要的温室气体之一[37]是破坏平流层臭氧层的主要因子[38],对全球气候和环境变化具有重要影响。与NH_3挥发量相比,N_2O排放量占施氮量的比例通常较低,平均值在1%左右[39-40]。化学氮肥的施用增加农田土壤N_2O排放[41],且有研究认为硝化作用过程是我国北方石灰性土壤N_2O产生的主导途径[42-43]。脲酶抑制剂在减少NH_3挥发的同时,也会影响硝化作用及后续反硝化作用速率[9]。因此,脲酶抑制剂配施尿素可能是降低N_2O排放的重要措施之一(表1)。Ding等[44]对华北平原农田土壤玉米种植季的研究表明,与单施尿素相比,增施NBPT可减少37.7%的N_2O排放。Dawar等[45]在牧场土壤中发现,NBPT与尿素配施后能够显著降低N_2O排放。Martins等[46]在热带土壤中发现,NBPT能够通过抑制NH_3挥

表1 脲酶抑制剂对土壤N_2O排放的影响

Table 1 Influences of urease inhibitors on soil N_2O emissions

脲酶抑制剂 Urease inhibitors	土壤质地 Soil texture	土壤pH Soil pH	土壤黏粒含量 Clay content	氮素种类及施用量 N source and application rate/(kg·hm^{-2})	N_2O损失量 N_2O losses/(kg·hm^{-2})	N_2O排放量变幅 Change rates of N_2O emission	监测期 Periods of detection/d	参考文献 References
NBPT	沙壤土	8.6	11%	尿素200	0.48	−38%	115	[44]
NBPT	粉砂壤土	5.7	—	尿素100	0.39	−7.1%	63	[45]
NBPT	砂质黏壤土	6.1	21%	尿素150	6.00	−25%	220	[46]
NBPT	黏壤土	7.8	38%	尿素600	2.41	−28%	365	[47]

注：表中氮素施用量和N_2O损失量以N计。下同。

Note: The amount of N application and N_2O losses is calculated in nitrogen. The same below.

发来减少N_2O的间接排放。Zhao等[47]对石灰性土壤小麦-玉米轮作体系连续3年的田间监测结果显示，与单施尿素相比，尿素配施NBPT在玉米、小麦生长季和全年均显著降低了N_2O排放。这可能主要与脲酶抑制剂NBPT延缓尿素水解、降低土壤NH_4^+浓度有关；另一方面，作物氮肥利用率的提高也会降低硝化和反硝化作用底物NH_4^+和NO_3^-浓度，进而减少N_2O排放。

Fan等[48]基于荟萃分析发现，土壤pH是影响NBPT降低N_2O排放的关键因素，NBPT在碱性土壤中显著降低了N_2O排放，而在酸性土壤中则无明显影响。多数情况下尿素添加脲酶抑制剂后土壤N_2O排放降低或差异不显著[49]，但也有研究发现添加脲酶抑制剂后增加了N_2O的排放[37]。这可能是由于土壤初始NO_3^-含量和含水量较高，易于反硝化作用过程进行，尿素水解并未直接影响N_2O排放。

1.2.3 对硝酸盐淋洗的影响

硝酸盐(NO_3^-)可引起地表水富营养化，若饮用水中NO_3^-含量较高还会危害人体健康。NO_3^-的淋洗与土壤中NO_3^-含量呈显著正相关[50]。化学氮肥和有机肥的大量施用导致农田土壤NO_3^-明显累积，增加了NO_3^-淋洗至地下水的风险[51-52]。降低硝化作用速率或减少硝化作用初始底物NH_4^+浓度，是避免土壤NO_3^-大量淋洗的有效途径之一。Sanz-Cobena等[53]在地中海气候条件下连续2年监测玉米季土壤发现，与单施尿素相比，NBPT减少了NO_3^-淋洗约18%。周旋等[54]在黄泥田水稻土壤中研究结果显示，尿素和尿素硝铵配施NBPT降低了淋洗液NO_3^-累积量的15.6%。Zaman等[11]在牧场土壤的田间试验表明，尿素添加NBPT降低淋洗液中47%的NO_3^-。类似地，Dawar等[55]在牧场土壤中也发现，尿素和尿素+NBPT处理总NO_3^-损失量分别为3.83、2.46 kg·hm^{-2}(以N计)，添加NBPT减少了36%的NO_3^-损失。这主要是因为脲酶抑制剂NBPT减缓了尿素的水解，降低了NH_4^+浓度，进而限制了硝化作用速率和NO_3^-的供给。

1.2.4 对作物氮肥利用率和产量的影响

脲酶抑制剂在降低氮素损失的同时，也一定程度地提高了作物氮肥利用率(NUE)，这将有利于促进作物产量的提升(表2)。Abalos等[57]基于荟萃分析的研究表明，脲酶/硝化抑制剂使NUE平均提高12.9%。张文学等[58]在水稻土壤中研究发现，与仅施用尿素处理相比，添加NBPT后水稻地上部氮素回收率提高幅度为19.4%。Suter等[59]研究发现，添加脲酶抑制剂促进了土壤中氮的固存。玉米盆栽试验表明，NBPT与尿素协同施用后的NUE为47.9%，较单施尿素处理增加幅度为18.6%[60]。施用NBPT能够提高棉花产量、

表2 脲酶抑制剂对作物产量的影响

Table 2 Influences of urease inhibitors on crop yield

脲酶抑制剂 Urease inhibitors	土壤质地 Soil texture	作物 Crops	水分投入量 Water input/mm	氮素种类及施用量 N source and application rate/(kg·hm^{-2})	产量 Yield/(t·hm^{-2})	产量变幅 Change rates of yield	监测期 Periods of detection/d	参考文献 References
NBPT	黏壤土	小麦-玉米	688	尿素600	15.6	+9.1%	365	[47]
NBPT	沙壤土	牧场	—	尿素150	11.1	+17%	70	[11]
NBPT	沙壤土	玉米	850	尿素250	14.5	+7.9%	162	[52]
NBPT	黏壤土	玉米	605	尿素130	9.94	+3.33%	150	[56]
NBPT	黏壤土	玉米	605	尿素硝铵130	11.7	+9.35%	150	[56]

氮素吸收量和NUE，且与仅施用尿素处理相比，添加NBPT后NUE增加了16.8个百分点[61]。这主要是因为施用脲酶抑制剂在延缓尿素水解并减少NH_3挥发的同时，也利于土壤氮素持续供应，更好地满足作物对氮素的需求[62]，进而提高作物对氮素的吸收利用。Huang等[63]对中国农田土壤进行荟萃分析发现，脲酶抑制剂整体增加作物产量约4.7%。Linquist等[64]研究发现，脲酶抑制剂施用后水稻产量平均增加5.7%。与单施尿素处理相比，NBPT配施尿素使作物产量平均增幅达5.3%[18]。Cantarella等[26]综合96个监测结果发现，施用NBPT后小麦、牧草、大米、大麦、豆类、玉米、棉花和甘蔗的产量平均提高10.2%、8.4%、7.6%、6%、5.2%、4.1%、1.8%和−0.8%。

脲酶抑制剂对不同作物增产效果的差异可能与作物生长周期及其氮素营养特性和土壤温度、pH、降雨量等其他环境因素有关。NBPT配施尿素处理水稻产量随降雨增加呈非线性递减趋势，同时与仅施用尿素处理相比，添加NBPT可使水稻产量增加8.9%~18.1%[65]。在热带强淋溶土中，NBPT配施尿素后玉米产量为7.17 t·hm^{-2}，较单施尿素处理提高约10%[66]。Drury等[56]研究发现NBPT配施后玉米产量增加了3.33%~9.35%。Chatterjee[67]研究表明，NBPT和尿素协同施用后显著增加冬小麦和甜菜产量，增幅分别为4.46%和6.23%。脲酶抑制剂在增加作物产量的同时，通常也会提高作物品质。盆栽条件下NBPT配施尿素能提高28.3%~33.7%的油菜生物产量，并降低植株体内4.2%~32.6%的硝酸盐含量[68]。与单施尿素（300 kg·hm^{-2}，以N计）处理相比，田间添加NBPT的尿素处理土豆产量增加42%，且以大果（>55 mm）和中果（35~55 mm）增产为主[69]。类似地，NBPT配施尿素的处理小麦产量可增加15.4%，同时增加小麦蛋白10.1%[70]。然而，也有研究显示脲酶抑制剂并没有显著提高作物的品质。如Bryant等[71]研究结果表明，施用包膜NBPT的尿素并未使水稻籽粒中蛋白含量提高，反而略有降低。试验结果的不一致可能与水稻中蛋白含量受氮肥种类和水稻品种基因型影响有关[72]。

2　硝化抑制剂

2.1　作用机理

硝化作用是全球土壤氮循环的关键过程，其氨氧化过程是该反应的限速步骤。参与该过程的土壤微生物主要是自养的AOB和AOA，且通常认为在中性、碱性和高氮投入或氮充裕的土壤条件下AOB是驱动硝化过程进行的主体，而在酸性、氮含量相对较低的自然生态系统中AOA发挥更为重要的作用[73]。氨在氨氧化菌氨单加氧酶（AMO）作用下被氧化为羟胺（NH_2OH），随后在羟胺氧化还原酶（HAO）作用下氧化为亚硝酸（NO_2^-）[14]。大多数硝化抑制剂通过抑制AMO活性来减缓硝化作用进程（图1）。其主要抑制作用机理：①直接与AMO结合并相互作用，如硝基吡啶；②螯合AMO中的辅酶因子Cu，降低其有效性，如DMPP；③底物氧化使AMO失活，如乙炔。一般认为硝化抑制剂主要通过抑制氨氧化细菌微生物的活性来暂时阻止NH_3氧化为羟胺（图1），进而延长NH_4^+在土壤中的滞留时间[74]，减缓硝化作用进程并降低该过程中N_2O排放，同时也降低了土壤中NO_3^-浓度及其淋洗风险[75]。因此，硝化抑制剂被推荐为减少农田土壤N_2O排放的重要措施之一[76]，并被广泛应用在各农业系统中[77]。

目前，DCD和DMPP是最为常见并已商业化应用的硝化抑制剂。有研究表明，DCD具有抑菌作用而非杀菌功能，其主要通过暂时阻碍AOB的生长和活性，限制其对NH_4^+的吸收和利用[78]。DCD降解或抑制效能下降后，土壤AOB将逐渐恢复活性并重新进行氨氧化过程。但也有研究发现，酸性土壤中一定浓度的DCD可完全抑制AOA的生长[79]。与DCD相比，DMPP能够通过螯合AMO中的Cu来阻碍AOB对NH_3的氧化反应，高效抑制AOB生长和相关*amoA*基因的表达[80–81]，但对AOA并无影响[82–83]。Shi等[84]在菜田和草地土壤上的对比试验表明，DMPP通过影响AOB的丰度和代谢活性有效抑制碱性菜田土壤的硝化作用和N_2O排放，而对酸性草地土壤的硝化作用和硝化菌影响不显著，这与酸性土壤AOB丰度较低以及DMPP作为一种杂环化合物可能被有机质所吸附，从而降低对氨氧化过程的有效抑制有关。同时，Li等[85]研究发现，DMPP可直接抑制氨氧化和反硝化微生物活性进而有效抑制N_2O的排放。Dong等[86]在大豆–玉米轮作系统中的研究结果表明，在培养49 d后DMPP配施尿素显著降低了*nirS*基因丰度。Kou等[87]在设施菜田土壤中研究发现，DMPP显著减少了*nirS*和*nirK*基因拷贝数，而DCD对其无影响。DMPP对不同细菌种群的影响依赖于土壤含水量，40% WFPS（土壤孔隙含水量）条件下施用DMPP降低了*amoA*、*narG*、*nirK*和*nosZ*基因丰度，而在80% WFPS条件下，DMPP对*amoA*基因丰度无显著影响，但增加了反硝化菌基因丰度[88]。然而，早期研究发现，DMPP并未影响土壤硝酸盐还

原酶和N_2O还原酶活性，这可能与施用氮肥的形态和土壤环境条件有关[89]。

2.2 环境和农学效应

2.2.1 对NH_3挥发的影响

与脲酶抑制剂不同，硝化抑制剂延长NH_4^+在土壤中的滞留时间，通常会增加NH_3排放潜势[77,90]。多数研究表明，施用硝化抑制剂将增加土壤NH_3挥发损失量（表3）。Qiao等[77]综合62个田间施用硝化抑制剂试验结果发现，施用硝化抑制剂增加了NH_3的排放，平均增幅为20%。同时，Lam等[94]整合文献结果显示，硝化抑制剂增加NH_3挥发损失量0.2~18.7 kg·hm^{-2}（以NH_3-N计）。室内培养试验结果表明，施用DCD可增加5%~16%的NH_3挥发损失，同时DCD与NBPT配施能够部分抵消NBPT对减少NH_3挥发的有利效应[35]。在菜田种植系统中，施用有机肥后NH_3挥发迅速增加，与仅施用有机肥处理相比，添加DMPP使NH_3损失增加37%[91]。与单独施用尿素或有机肥处理相比，温室土壤添加DCD的尿素或有机肥处理在15 d内累积的NH_3排放量分别显著增加了58%和38%[92]。在稻田土壤中，与单施尿素处理相比，添加DMPP后NH_3挥发累积量增加了7.2%[27]。与单施尿液处理相比，添加DCD在春季和秋季牧场土壤中NH_3挥发损失的增幅分别为16%和39%[95]。然而，也有研究表明，与仅施用牛粪相比，尽管添加DMPP处理的NH_3挥发损失量增加42%，但二者差异并不显著；同时硫硝酸铵添加DMPP后甚至使NH_3的损失量降低[93]。

2.2.2 对温室气体N_2O排放的影响

硝化抑制剂在降低土壤N_2O排放方面具有良好的效果（表4）。Qiao等[77]综合田间应用硝化抑制剂的试验结果发现，硝化抑制剂的施用平均减少N_2O排放达44%。Fan等[96]在陕西和山东两地菜田土壤中研究发现，添加硝化抑制剂DCD后N_2O排放量分别降低了61%和46%。Zhang等[97]在菜田土壤中也发现，与仅施用尿素处理相比，添加DCD可减少田间6.2%的N_2O排放。Shamsuzzaman等[98]开展的尿素与不同有机物料配比的研究结果显示，尿素+水稻秸秆、尿素+牛粪和尿素+鸡粪处理添加DCD后，土壤N_2O排放量分别降低了40.6%、43.4%和24.5%。Dai等[99]在牧草土壤中研究发现，DCD施用后N_2O排放总量减少52%~69%，主要归因于DCD抑制了土壤AOB的生长。与DCD相比，DMPP的施用量仅为DCD的1/10，同时，连续3年的试验结果表明DMPP降低了49%的N_2O排放量，而DCD仅降低了26%[100]。类似地，在设施菜田土壤也发现DMPP对减少N_2O排放、延缓氨氧化的效果均优于DCD[87]。在草地土壤中施用DMPP能显著减少23%~33%的N_2O累积排放量[101]。在小麦-玉米轮作农田土壤中，尿素和尿素+DMPP处理N_2O年累积

表3 硝化抑制剂对土壤NH_3挥发损失的影响

Table 3 Influences of nitrification inhibitors on soil NH_3 volatilization

硝化抑制剂 Nitrification inhibitors	土壤质地 Soil texture	土壤pH Soil pH	土壤黏粒含量 Clay content	氮素种类及施用量 N source and application rate/(kg·hm^{-2})	NH_3损失量 NH_3 losses/(kg·hm^{-2})	NH_3损失变幅 Change rates of NH_3 loss	监测期 Periods of detection/d	参考文献 References
DMPP	沙土	7.9(土水比1:5)	<9%	鸡粪有机肥255	27	+37%	24	[91]
DCD	细沙壤土	5.7(土水比1:2.5)	12%	尿素90	9.89	+58%	15	[92]
DCD	细沙壤土	5.7(土水比1:2.5)	12%	有机肥90	3.47	+38%	15	[92]
DMPP	黏壤土	6.6(土水比1:2)	29%	硫硝酸铵97	0.14	−52%	5	[93]
DMPP	黏壤土	6.6(土水比1:2)	29%	牛粪181	10.7	+42%	5	[93]

注：表中NH_3损失量以N计。

Note: The amount of NH_3 losses is calculated in nitrogen.

表4 硝化抑制剂对土壤N_2O排放的影响

Table 4 Influences of nitrification inhibitors on soil N_2O emissions

硝化抑制剂 Nitrification inhibitors	土壤质地 Soil texture	土壤pH Soil pH	土壤黏粒含量 Clay content	氮素种类及施用量 N source and application rate/(kg·hm^{-2})	N_2O损失量 N_2O losses/(kg·hm^{-2})	N_2O排放量变幅 Change rates of N_2O emission	监测期 Periods of detection/d	参考文献 References
DCD	黏壤土	7.8	38%	尿素600	1.55	−54%	365	[47]
DCD	沙壤土	8.6	11%	尿素200	0.47	−39%	115	[44]
DMPP	黏壤土	6.6(土水比1:2)	29%	硫硝酸铵97	4.05	−8.8%	59	[93]
DMPP	黏壤土	6.6(土水比1:2)	29%	牛粪181	11.0	−29%	59	[93]

排放量分别为4.49、2.78 kg·hm^{-2}（以N计），即DMPP减少了38%的N_2O年排放量[102]。室内培养试验结果表明，与单施尿素处理相比，DMPP在石灰性土壤中（pH 7.9）减少N_2O累积排放量高达99.2%[103]。可见，在碱性条件下DMPP对土壤硝化作用具有较高的抑制率[104]。与DMPP相比，DCD可在酸性土壤条件下显著降低N_2O排放量，而对中性和碱性土壤无显著影响[105]。

通常，硝化抑制剂在降低N_2O排放的同时会增加NH_3挥发损失（见2.2.1）。尽管NH_3本身并不是温室气体，但其是N_2O间接排放的重要来源之一[106]。有研究发现，挥发损失的NH_3约有1%~5%经大气沉降、硝化和反硝化过程再次转化为N_2O[107]。这意味着硝化抑制剂对N_2O的减排效应将随NH_3排放量的负面效应的增强而相对减弱。考虑大气沉降的NH_3对N_2O的间接排放贡献，硝化抑制剂对N_2O排放的影响总体表现为-4.5~0.5 kg·hm^{-2}（以N_2O-N计）[94]。因此，未来研究应综合考虑硝化抑制剂对NH_3挥发导致的N_2O间接排放影响，以进一步准确综合评估和量化硝化抑制剂对N_2O的减排效应。此外，在土壤含水量较高（85%WFPS）的草地土壤中，与仅施用硫酸铵相比，DMPP施入增加了16.4%的分子态氮气（N_2）损失[108]。而Friedl等[109]的研究结果显示，添加DMPP减少牧场土壤70%以上的累积N_2损失，这可能与DMPP限制了反硝化底物NO_3^-有效性并减少了异养呼吸造成的氧气消耗有关。因此，硝化抑制剂对分子态氮气损失及反硝化作用的影响还需要进一步深入探究。

2.2.3 对硝酸盐淋洗的影响

硝化抑制剂的使用是减少土壤NO_3^-淋洗的重要措施之一。大样本分析数据表明，硝化抑制剂平均可显著减少47%的NO_3^-淋洗量[77]，这与Cai等[110]的研究结果一致，其发现DCD能够减少草地动物尿斑46%的NO_3^-淋洗量。与仅施用动物尿液处理相比，添加DCD在秋季和春季分别减少76%和42%的NO_3^-淋洗量[111]。类似地，Monaghan等[112]发现，草地土壤中施用DCD每年可平均减少NO_3^-损失21%~56%。同时，Welten等[113]研究结果表明，随DCD施用量的增加，草地土壤NO_3^-的淋洗总量下降，且显著降低了NH_4^+和可溶性有机氮（DON）的淋洗。进一步研究显示，草地土壤总NO_3^-的淋洗损失与AOB的*amoA*基因拷贝数和硝化速率显著相关，而与AOA无相关性[114]。在太湖地区水稻油菜轮作体系下，尿素和尿素+DMPP处理NO_3^-损失量分别为21.4、10.8 kg·hm^{-2}（以N计），即DMPP显著降低了NO_3^-淋洗[115]。在菜田土壤中，尿素和有机肥添加DCD后可分别使NO_3^-淋洗量降低77%和80%，但增加了NH_4^+淋洗风险[92]。Cui等[116]在集约化菜田土壤中发现，施用DCD能降低36.2%~58.5%的NO_3^-淋洗量。与仅施用尿素处理相比，DMPP与尿素混施后显著增加小麦-玉米轮作体系土壤pH和NH_4^+浓度，并降低NO_3^-+NO_2^-含量[117]。综上可见，硝化抑制剂的施用可有效减少土壤NO_3^-淋洗风险。此外，也有研究发现，硝化抑制剂可减少土壤中Ca^{2+}、Mg^{2+}和K^+等阳离子的淋洗损失[118-119]以及牧草中NO_3^-含量[120]。

2.2.4 对作物氮肥利用率和产量的影响

硝化抑制剂在降低土壤NO_3^-淋洗和N_2O排放的同时，还可提高作物产量（表5）和NUE（表6）。在尿素施氮量较低（23 kg·hm^{-2}，以N计）条件下，添加DMPP可增加32%的牧草干质量[125]。Li等[115]在水稻-油菜轮作区发现，DMPP与尿素协同施用后均显著增加水稻和油菜籽的产量，产量增幅分别为5.3%和6.9%。Zhao等[47]在华北平原小麦-玉米轮作体系2013—2014年间的研究结果显示，与仅施尿素处理相比，添加DCD尿素处理的小麦和玉米产量分别为6.7、8.9 t·hm^{-2}，年平均增幅为9.1%。类似地，尿素配施DCD后小麦产量增加了7.9%[121]。不同地域菜田土壤试验结果表明，在湖南强淋溶土、陕西塿土、山东潮土、黑龙江黑土中添加DCD的尿素处理蔬菜产量分别增加3.1%、6.6%、17.5%和17.6%[91]。DMPP显著增加晚稻产量，平均增幅为15.1%，但对早稻无显著增产作用[126]。DMPP与氮肥配施后显著增加萝卜和生

表5 硝化抑制剂对作物产量的影响

Table 5 Influences of nitrification inhibitors on crop yield

硝化抑制剂 Nitrification inhibitors	土壤质地 Soil texture	作物 Crops	水分投入量 Water input/mm	氮素种类及施用量 N source and application rate/(kg·hm^{-2})	产量 Yield/(t·hm^{-2})	产量变幅 Change rates of yield	监测期 Periods of detection/d	参考文献 References
DCD	沙壤土	小麦	170	尿素120	4.37	+7.9%	130	[121]
DCD	黏壤土	小麦-玉米	688	尿素600	15.7	+9.8%	365	[47]
DMPP	黏壤土	水稻-油菜	—	尿素180	11.0	+5.77%	240	[115]
DMPP	—	小麦-玉米	1 074	尿素430	14.2	+9.23%	365	[102]

表6 硝化抑制剂对氮肥利用率的影响

Table 6 Influences of nitrification inhibitors on nitrogen utilization efficiency (NUE)

硝化抑制剂 Nitrification inhibitors	土壤质地 Soil texture	作物 Crops	水分投入量 Water input/mm	氮素种类及施用量 N source and application rate/(kg·hm^{-2})	氮肥利用率 NUE/%	氮肥利用率变化百分点 Percent point changes of NUE	参考文献 References
DCD	沙壤土	西红柿	364	尿素210	20.7	+6.83	[122]
DCD	壤土	小麦-玉米	941	尿素160	36.8	+9.21	[123]
DCD	壤土	小麦-玉米	941	尿素220	35.9	+6.23	[123]
DCD	黏壤土	小麦-玉米	688	尿素600	37.5	+4.34	[47]
DMPP	粉质壤土	早稻	—	尿素165	42.5	+9.19	[124]
DMPP	粉质壤土	晚稻	—	尿素165	47.2	+9.95	[124]

菜产量,而对洋葱和菠菜产量无明显影响,甚至有降低趋势[127]。这可能与土壤环境条件、作物种类和生长周期不同等有关。例如,硝化抑制剂在酸性土壤中的NUE显著高于中性和碱性土壤,这可能与硝化抑制剂在中性和碱性土壤更易增加NH_3挥发损失有关[128]。大多数研究表明,硝化抑制剂施用在增加作物产量的同时,也会提高作物品质。与习惯施肥相比,施用含DCD的水溶肥可增加黄瓜中26%的可溶性糖含量,减少温室黄瓜硝酸盐含量达21.6%[129]。DCD与氮肥协同配施也可增加日光温室番茄近20%的产量,并显著降低番茄果实中的硝酸盐含量[130]。与DCD类似,DMPP可降低菠菜中26%~84%的硝酸盐含量[131],且施用含DMPP的复合肥可显著增加黄瓜、西瓜产量,提高可溶性糖、维生素C和氨基酸含量[132]。然而,施用硝化抑制剂也会产生一些负面效应。Yu等[119]研究发现DMPP尽管增加冬小麦的产量,却显著降低了冬小麦中粗蛋白含量。此外,2012年在新西兰发现,常年施用硝化抑制剂DCD的干草中存在DCD残留,并已在部分乳制品中检测到DCD,这极大增加了人们对食品安全的担忧[131]。

农田土壤较低的NUE主要归因于与硝化作用相关的氮素损失,如硝酸盐的淋洗和反硝化作用[133]。因此,利用硝化抑制剂抑制NH_4^+向NO_2^-的转化,有助于降低土壤NO_3^-的淋洗并提高作物NUE。Raza等[123]发现在尿素施氮量为220 kg·hm^{-2}(以N计)时,尿素和尿素配施DCD处理的小麦NUE分别为31.2%和38.1%。在不同尿素施氮量下,与仅施用尿素处理相比,尿素配施DMPP处理冬小麦NUE提高4.9~20.1个百分点,同时随着氮肥施用量的增加,DMPP对冬小麦NUE的提升作用逐渐下降[134]。在水稻氮肥利用率的研究中发现,连续两年试验中尿素和尿素+DMPP处理NUE均值分别为35%和45%[124]。在针对油菜的研究中发现,尿素和尿素+DCD处理NUE分别为30.7%和56.9%[135]。也有研究发现菜田土壤中添加DCD并未显著提高NUE[42]。与仅施用尿素相比,尿素配施DCD使番茄NUE增加6.83个百分点[122]。在草地土壤中,施用DCD使NUE明显增加[136]。不同农业生态系统中,硝化抑制剂对作物NUE的影响与作物种类及生长周期、抑制剂种类、肥料类型及施用量、土壤温度和水分等环境因子有关。

3 结论与展望

3.1 结论

(1)许多研究已证实,脲酶抑制剂与尿素或有机肥配合施用后能够降低土壤中NH_3挥发、N_2O排放和NO_3^-淋洗等形式的氮损失,并提高作物产量、品质及氮肥利用率。

(2)硝化抑制剂DCD和DMPP均能降低土壤N_2O排放和NO_3^-淋洗,并提高作物产量,但极易增加土壤NH_3挥发。

(3)不同农田生态系统中脲酶/硝化抑制剂的环境和农学效应与抑制剂种类、氮肥类型和用量、降雨或灌溉量、pH、黏粒含量等土壤理化参数有关。

3.2 展望

当前,对氮素增效剂的相关研究大多基于短期的试验结果,有必要开展长期定位试验,系统深入探究其对NH_3挥发、N_2O排放、NO_3^-和DON淋洗以及作物产量和品质的影响,并结合最新的分子生物学技术深入研究土壤微生物功能和群落结构以及土壤动物对长期施用脲酶/硝化抑制剂的响应。

脲酶/硝化抑制剂的研究大多集中于尿素水解和氨氧化过程,但对田间反硝化过程及其N_2O/N_2产物比的影响认知尚不清楚,应进一步分析抑制剂对分子态氮气排放的影响。

现阶段，尽管脲酶抑制剂和硝化抑制剂以及二者复配在化学氮肥中的实际应用逐渐增加，但由于抑制剂本身的化学稳定性有限，并未实现其与动物粪肥的商业化结合。与化学氮肥相比，有机肥造成的NH_3挥发、N_2O排放和NO_3^-淋洗通常较高，未来抑制剂与有机肥如何实现稳定结合可能是重要的研究方向之一。

此外，进一步研究开发对环境友好、对植物毒性低、化学性质稳定并具有成本竞争力的新型氮素抑制剂也十分必要。目前，氮素增效剂大多为化工合成产物，从生态环境和人体健康的角度考虑，生物硝化抑制剂将会是未来发展的新方向。

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