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Source: Canadian Journal of Soil Science, 101(2) : 192-202

Published By: Canadian Science Publishing

URL: https://doi.org/10.1139/cjss-2020-0044

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ARTICLE

Kinetics and thermodynamics of urea hydrolysis in the presence of urease and nitrification inhibitors

Ahmed A. Lasisi and Olalekan O. Akinremi

Abstract: Urease inhibitor [*N*-(*n*-butyl) thiophosphoric triamide (NBPT)] and nitrification inhibitor (NI) (3,4-dimethylpyrazole phosphate) have been used to reduce nitrogen (N) losses from urea-based fertilizers. This study evaluated the effect of temperature, NBPT, and NI on kinetic and thermodynamic properties of urea hydrolysis in six soils. Soils were amended (250 kg N·ha^{-1}) with urea (UR), NBPT treated urea (UR_{NBPT}), or NBPT + NI treated urea (UR_{DI}), incubated at 5, 15, or 25 °C, and destructively sampled eight times during an 18 d incubation. We measured urea hydrolysis rate by the disappearance of urea with time and determined the rate constant (*k*; d^{-1}) assuming first-order kinetics. Our results showed that *k* increased with temperature in the order of 0.07 (5 °C), 0.12 (15 °C), and 0.20 (25 °C) across soils and inhibitor treatments. In addition, *k* declined in the order of UR (0.19) > UR_{DI} (0.11) > UR_{NBPT} (0.08) across soils and temperatures. Although urease inhibitor, NBPT, increased the half-life of urea from 3.8 to 8.3 d across soil–temperature, the addition of a NI significantly reduced the half-life of NBPT treated urea by approximately 2 d across soil–temperature. Thermodynamics parameters showed that urea hydrolysis was nonspontaneous, and enthalpy and entropy changes were not significantly different among inhibitor treatments in five of the six soils. We conclude that the often-reported greater ammonia volatilization from UR_{DI} than UR_{NBPT} may not only be due to the persistence of ammonium in the presence of NI but also because NI reduced the inhibitory effect of NBPT on urea hydrolysis.

Key words: urea, NBPT, nitrification inhibitor, hydrolysis.

Résumé : Pour réduire la quantité d'azote (N) que perdent les engrais à base d'urée, on recourt à un inhibiteur de l'uréase [*N*-(*n*-butyl) triamide thiophosphorique (NBPT)] et à un inhibiteur de la nitrification [3,4-diméthylpyrazole phosphate (NI)]. Les auteurs ont évalué l'effet de la température, du NBPT et du NI sur les propriétés cinétiques et thermodynamiques de l'hydrolyse de l'urée dans six sols. Les sols en question avaient été amendés (250 kg de N par ha) avec de l'urée (UR), de l'urée additionnée de NBPT (UR_{NBPT}) ou de l'urée traitée avec du NBPT et du NI (UR_{DI}), puis incubés à 5, 15 ou 25 °C et échantillonnés huit fois de façon destructive pendant les 18 jours de l'incubation. Les auteurs ont mesuré le taux d'hydrolyse de l'urée d'après la disparition de l'amendement dans le temps, puis ils ont déterminé la constante de vitesse (k; par jour) en présumant une cinétique du premier degré. Selon les résultats, la constante k augmente avec la température par un facteur de 0,07 (5 °C), 0,12 (15 °C) ou 0,20 (25 °C) pour tous les sols et les inhibiteurs. Par ailleurs, k diminue dans l'ordre UR (0,19) > UR_{DI} (0,11) > UR_{NBPT} (0,08) pour tous les sols et températures. Bien que l'inhibiteur de l'uréase NBPT prolonge la demi-vie de l'urée (de 3,8 à 8,3 jours) pour l'ensemble des sols et températures, l'addition de NI réduit sensiblement la demi-vie de l'urée traitée au NBPT (environ deux jours pour tous les sols et températures). Les paramètres thermodynamiques indiquent que l'urée ne s'hydrolyse pas de façon spontanée et que les changements au niveau de l'enthalpie et de l'entropie ne varient pas de façon sensible entre les deux inhibiteurs dans cinq des six sols traités. Les auteurs en concluent que la plus forte volatilisation de l'ammoniaque, souvent rapportée avec l'usage d'UR_{DI} plutôt que d'UR_{NBPT}, pourrait non seulement résulter de la persistance de l'ammonium en présence de NI, mais aussi de la diminution du pouvoir inhibiteur du NBPT sur l'hydrolyse de l'urée en présence de NI. [Traduit par la Rédaction]

Mots-clés : urée, NBPT, inhibiteur de la nitrification, hydrolyse.

Received 6 April 2020. Accepted 2 October 2020.

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Introduction

In agricultural and horticultural production, urea accounts for more than one-half of the global source of nitrogen (N) fertilizers. When urea is applied to soils, it hydrolyzes to ammonium (NH_4^+) with the aid of the ubiquitous urease enzyme. The hydrolysis of applied urea occurs in two stages (Zambelli et al. 2011). The first stage is the break down of urea by urease enzyme into NH_4^+ and carbamate ions. The second stage is the rapid decomposition of the carbamate ion into NH_4^+ and bicarbonate. The rate of urea hydrolysis increases with an increase in temperature as a result of an increase in urease activity (Cartes et al. 2009; Lei et al. 2018*a*). Urea hydrolysis results in an increase in soil pH around the urea granules, thereby subjecting the NH_4^+ produced to volatilization in form of ammonia (NH_3) (Overrein and Moe 1967). The magnitude of NH_3 volatilization from urea may be greater than 15% of applied urea-N when urea is surface applied without incorporation irrespective of the soil and environmental conditions (Cantarella et al. 2018; Lasisi et al. 2019). The volatilized NH_3 may be deposited on the soil surface with the potential to cause soil acidification or N enrichment of N limited ecosystem; or combined with acidic gases in the atmosphere to form particulate matters that are detrimental to human health (Aneja et al. 2008; Sheppard et al. 2010). In addition, NH_3 volatilization from urea fertilizers is an agronomic loss to farmers as a result of reduced N use efficiency of urea fertilizers.

The NH_4 formed during urea hydrolysis that is not volatilized may subsequently be converted to nitrate (NO_3) by a process known as nitrification or be taken up by crops or immobilized by soil microorganisms. The nitrification process is a microbial sequential transformation of NH_4^+ into NO_3 (Sahrawat 2008). Unlike the hydrolysis of urea, nitrification of NH_4^+ into NO_3 results in soil acidification (Subbarao et al. 2006). The decrease in soil pH may, in turn, reduce the rate of nitrification in soil (Zebarth et al. 2015; Hanan et al. 2016). The NH_4^+ and NO_3 are both desirable by plants for uptake even though the preference for each may differ by plants (Zebarth et al. 2015). Continuous accumulation of NO_3 in soil poses an environmental challenge of NO_3 leaching to the groundwater in the event of a large amount of rainfall (Zaman et al. 2008). In addition, unintended nitrous oxide emission to the atmosphere during the nitrification of NH_4^+ and denitrification of the produced NO_3 makes the process of nitrification less desirable (Wrage et al. 2001).

The use of urease inhibitor especially *N*-(*n*-butyl) thiophosphoric triamide (NBPT) has been reported to effectively reduce NH_3 volatilization by a global average of 52% from surface-applied urea (Silva et al. 2017; Cantarella et al. 2018). The reduction of NH_3 volatilization by NBPT is due to inhibition of urea hydrolysis through the reduction of urease activity (Christianson et al. 1993). To inhibit urease activity, NBPT is converted to *N*-(*n*-butyl) phosphoric triamide (NBPTO) or *N*-(*n*-butyl) thiophosphoric diamide (NBPD) (Creason et al. 1990; Mazzei et al. 2019). The NBPTO or NBPD hydrolyzes to diamido phosphoric acid or monoamido thiophosphoric acid, respectively, which then blocks the active sites (two nickel ions) of the urease enzymes; thereby preventing contact between the urease enzyme and urea (Mazzei et al. 2019). Although the rate of urea hydrolysis is slow at temperatures ≤5 °C, studies have shown that NH_3 volatilization was still greater from untreated urea than NBPT treated urea in cold soils (Engel et al. 2017; Lasisi et al. 2020*a*). In the case of a nitrification inhibitor (NI), the activity of ammonia-oxidizing organisms is inhibited by the NI (Subbarao et al. 2006). This allows applied N to persist longer in the NH_4^+ form in the soil. Common NI includes dicyandiamide, nitrapyrin, and 3,4-dimethylpyrazole phosphate (DMPP). The NBPT and NI are usually applied with N to maximize agronomic return while safeguarding the environment.

Several studies have reported that the addition of NI with NBPT [double inhibitor (DI)] on urea often interfere with the effectiveness of NBPT to reduce NH_3 volatilization (Gioacchini et al. 2002; Zaman et al. 2008; Soares et al. 2012; Frame 2017; Mariano et al. 2019; Lasisi et al. 2020*a*). The studies of Soares et al. (2012) and Frame (2017) found that the potential to increase NH_3 volatilization from DI-treated urea (UR_{DI}) relative to NBPT-treated urea (UR_{NBPT}) increased as the concentration of the NI increased. The greater NH_3 volatilization from UR_{DI} than UR_{NBPT} has been attributed to the persistence of NH_4^+ in the presence of the NI. However, a recent incubation study (conducted at 21 °C) clearly showed that the rate of urea hydrolysis was greater in UR_{DI} than UR_{NBPT} from four of five soils used in the study (Lasisi et al. 2020*b*). Previous studies have shown that the rate of urea hydrolysis with and without NBPT increased as the temperature increased (Suter et al. 2011; Engel et al. 2013). Nevertheless, there is a lack of information on the coupled effect of temperature, urease inhibitor, NBPT, and NI on the hydrolysis of urea. In addition, there is little information in the literature on the thermodynamic parameters such as activation energy (E_a), Gibb's free energy (ΔG), enthalpy change (ΔH), and entropy change (ΔS) of urea hydrolysis, particularly urea treated with NBPT or DI. The objective of our study was to evaluate the interactive effect of temperature, urease inhibitor (NBPT), and NI (DMPP) on the kinetic and thermodynamic parameters of urea hydrolysis.

Materials and Methods

Soil characteristics

This study was conducted with soils (0–15 cm) collected from six different sites in Manitoba, Canada. The location of the sites was Carman (CM; 49°29′6″N, 98°02′2″W), Carberry (CB; 49°53′7″N, 99°22′29″W), Deerwood (DW; 49°22′1″N, 98°23′34″W), High Bluff

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(HB; 50°01′2″N, 98°08′9″W), Portage la Prairie (PP; 49°57′9″N, 98°16′0″W), and Beausejour (BJ; 50°05′13″N, 96°29′58″W). The soils were air-dried, ground, and passed through a 2 mm sieve. Subsamples of the soils were collected to determine urease activity (Tabatabai and Bremner 1972), soil texture (Gee and Bauder 1986), electrical conductivity, pH (soil/water, 1:2), cation-exchange capacity (Hendershot et al. 2008), organic matter (Walkley and Black 1934), and available N (Maynard et al. 2008) (Table 1).

Table 1. Selected soil (0–15 cm) properties.

Property	Carman	Carberry	Deerwood	High Bluff	Beausejour	Portage
Soil classification[a]	Orthic Black Chernozem	Orthic Black Chernozem	Orthic Dark Gray Chernozem	Gleyed Cumulic Regosol	Gleyed Rego Black Chernozem	Gleyed Rego Black Chernozem
Soil series	Hibsin	Fairland	Dezwood	High Bluff	Dencross	Neurhorst
Soil pH_{water}	5.51	6.65	6.62	7.46	7.76	7.96
Electrical conductivity ($\mu S \cdot cm^{-1}$)	394	228	1853	899	1377	596
Organic matter ($g \cdot kg^{-1}$)	27	33	34	45	88	71
Available N ($mg \cdot kg^{-1}$)	31	15	186	58	22	82
Field capacity ($m \cdot m^{-3}$)	0.35	0.24	0.36	0.41	0.61	0.44
Urease activity (mg NH_4^+-$N \cdot kg^{-1}$ soil$\cdot h^{-1}$)	11	17	24	57	63	88
Cation-exchange capacity ($cmol \cdot kg^{-1}$)	16	14	23	28	47	36
Soil texture	Sandy loam	Sandy loam	Loam	Loam	Clay	Clay loam
Sand ($g \cdot kg^{-1}$)	711	764	465	427	108	269
Silt ($g \cdot kg^{-1}$)	123	128	318	325	322	343
Clay ($g \cdot kg^{-1}$)	166	108	217	248	570	388

[a]Soil classification is according to MAFRI (2010).

Experimental design and treatment applications

The experiment design was a randomized complete block design with a split-plot layout. The split-plot layout consisted of temperature as the main plot and factorial combination of soils by inhibitor treatments by sampling time as the subplot. The temperatures (replicated three times) were 5, 15, and 25 °C; soils were CM, CB, DW, HB, PP, and BJ; inhibitor treatments were untreated urea (UR), NBPT-treated urea (UR_{NBPT}), and NBPT + NI (DI) treated urea (UR_{DI}). We prepared UR_{NBPT} (360 mg NBPT$\cdot kg^{-1}$ urea) by coating urea with ARM U™ formulation (180 g NBPT$\cdot L^{-1}$) and UR_{DI} (360 mg NBPT + 90 mg DMPP$\cdot kg^{-1}$ urea) by coating urea with ARM U Advanced™ formulation (240 g NBPT + 60 g DMPP$\cdot L^{-1}$). Our sampling times were 0.5, 1, 2, 4, 7, 10, 14, and 18 d after fertilization. Due to a large number of the experimental units, replicates of each experimental unit were blocked with time.

Twenty-five grams of each air-dried soil (<2 mm) was weighed into a 30 mL cup (conical frustum shape with 4.6 cm top i.d., 3.0 cm base i.d., and 3.2 cm height; Medline Industries Inc., Northfield, IL, USA). The soils were wetted to 75% field capacity, covered, and left for 24 h at room temperature to allow soil and water to equilibrate. After 24 h, we applied 50 mg (250 kg N$\cdot ha^{-1}$ on soil mass basis) of inhibitor treatment (as granular urea treated with or without inhibitor) to the centre of the soil surface. The cups were arranged on a tray containing water and set in an incubator at a temperature of 5, 15, or 25 °C. Water on the tray helped to reduce the rate of evaporation from the soil surface and kept the incubator relatively humid. Each incubator contained soil (6) by inhibitor treatment (3) by sampling time (8) cups. Every 2 d, three random cups of each soil by inhibitor treatment by temperature were weighed to determine moisture loss. The difference in mass (as a result of moisture loss) was adjusted by adding de-ionized water to the edge of the cups with a pipette.

Soil sampling and analysis

At each sampling time, a set of samples (six soils × three inhibitor treatments × three temperatures for a total of 54 samples) was destructively sampled for extraction and analysis. Soils in each cup were transferred (by putting the cup and soil) into a 1 L jar containing

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250 mL of 1 mol·L^{-1} KCl-phenylmercuric acetate and placed on a reciprocating shaker for 60 min. After 60 min, the samples were filtered (Whatman No. 40) into a 25 mL scintillating vials and refrigerated. The filtrate was analyzed colorimetrically for urea-N (Mulvaney and Bremner 1979). Ammonium and NO_3 concentrations from the filtrate were analyzed with AQ2 Discrete Analyzer (SEAL Analytical Inc., Mequon, WI, USA).

The urea-N measured in each soil was expressed as a percent of applied urea-N. The hydrolyzed urea was calculated as the disappearance of urea-N with time (eq. 1):

$$U_{\text{hyd}} = U_0 - U_t \quad (1)$$

where U_{hyd} is the hydrolyzed urea-N, U_0 is the amount of urea-N applied, U_t is the amount of urea-N recovered (% of applied urea-N) at time t, and t is the time or day after the start of the incubation (d).

Change in inorganic N concentration (NH_4^+-N + NO_3^--N) in each soil was calculated (Li et al. 2018; Wang et al. 2019) as

$$\Delta \text{IN}_t = \text{IN}_t - \text{IN}_i \quad (2)$$

where ΔIN_t is the change in NH_4^+-N or NO_3^--N concentrations (mg·kg^{-1}) at time t, IN_t is the NH_4^+-N or NO_3^--N concentrations (mg·kg^{-1}) measured from the soil at time t of the experiment, and IN_i is the NH_4^+-N or NO_3^--N concentrations (mg·kg^{-1}) measured from the soil before the start of the study.

Kinetics, thermodynamics, and statistical analysis

We performed all model fittings and statistical analyses with SAS software (SAS Institute Inc. 2014; version 9.4). All model fittings were performed by replicates for each soil × inhibitor treatment × temperature experimental unit. We fitted different kinetic equations (first- and zero-order, first-order, first- plus linear-order, and hyperbolic models) with PROC NLIN to generate urea hydrolysis rate constant (k), and we found the first-order kinetic model to best fit the data based on the lowest Akaike's information criterion (Archontoulis and Miguez 2015). Previous studies have reported the first-order kinetics to effectively describe urea hydrolysis rate under various soil and environmental conditions (Rodriguez et al. 2005; Lei et al. 2018*a*). The first-order kinetic equation used was as follows:

$$U_{\text{hyd}} = U_0[1 - \exp(-kt)] \quad (3)$$

Parameters are as defined above.

The k, the first-order kinetic constant, determined from eq. 3 was used to calculate half-life ($t_{1/2}$) and Q_{10} as follows:

$$t_{1/2} = \frac{\ln 2}{k} \quad (4)$$

$$Q_{10} = \left(\frac{k_a}{k_b}\right)^{[10/(T_a - T_b)]} \quad (5)$$

where k_a and k_b are first-order kinetic rate constants at 5 and 15 °C, respectively, or 15 and 25 °C, respectively, T_a and T_b are incubation temperatures at 5 and 15 °C, respectively, or 15 and 25 °C, respectively.

The k dependence on temperature was used to determine the thermodynamic parameters of urea treated with and without inhibitors in soils. The thermodynamic parameters determined were activation energy (E_a), change in Gibb's free energy (ΔG), enthalpy change (ΔH), and entropy change (ΔS). The E_a (KJ·mol^{-1}) for each soil by inhibitor treatment was determined with PROC NLIN using the Arrhenius equation (eq. 6):

$$k = Ae^{-E_a/RT} \quad (6)$$

where T is the temperature in Kelvin (K), R is the gas constant (8.314 J·mol^{-1}·K^{-1}), and A is a pre-exponential factor.

In addition, the ΔG (KJ·mol^{-1}) for each soil by inhibitor treatment was determined with PROC NLIN using the Van't Hoff equation (eq. 7).

$$K_e = e^{-\Delta G/RT} \quad (7)$$

where K_e is the equilibrium constant. Because urea hydrolysis is not a chemical equilibrium reaction, the absolute reaction-rate or transition-state theory of the relationship between k and K_e (Glasstone et al. 1941; Kumar and Wagenet 1984; Lei et al. 2018*b*) was used to rewrite the Van't Hoff equations as follows:

$$K_e = \frac{N_o k h}{nRT} \quad (8)$$

where N_o is the Avogadro's constant, h is the Plank's constant (6.6261×10^{-34} J s), and n is the number of moles. But N_o and R are related via Boltzman constant (k_b; 1.3806×10^{-23} J·K^{-1}) as shown in eq. 9.

$$nRT = N_o k_b T \quad (9)$$

Then,

$$k = \left(\frac{k_b T}{h}\right) e^{-\Delta G/RT} \quad (10)$$

To determine ΔH and ΔS, the ΔG for each soil and inhibitor treatment at each temperature was calculated using eq. 10, and linear regression with PROC REG was used to estimate ΔH (intercept) and ΔS (slope) using their relationship in eq. 11.

$$\Delta G = \Delta H - T\Delta S \quad (11)$$

Analysis of variance (ANOVA) with repeated measure analysis in PROC GLIMMIX was used to determine the effect of temperature and inhibitor treatment on

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Table 2. Effect of temperature, inhibitor treatment, and time on urea-N recovered, Δ in ammonium-N concentration, and Δ in nitrate-N concentrations in each soil.

	Probability values					
Model effect	Carman	Carberry	Deerwood	High Bluff	Beausejour	Portage
Urea-N recovered						
Temperature (*T*)	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Inhibitor treatments (*I*)	0.0016	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Time (*t*)	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
$T \times I$	0.4043	0.1645	0.0510	0.7154	0.8917	0.9937
$T \times t$	<0.0001	<0.0001	<0.0001	<0.0001	0.3743	0.7865
$I \times t$	0.8154	<0.0001	<0.0001	0.0054	0.0013	0.0171
$T \times I \times t$	0.7089	0.0003	0.0480	0.1966	0.6501	0.9350
Ammonium-N concentrations						
T	<0.0001	0.0197	0.3300	0.0281	0.0048	0.0515
I	0.4693	0.0444	<.0001	0.0258	0.0039	0.1473
T	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
$T \times I$	0.9875	0.2995	0.0025	0.9992	0.9312	0.8473
$T \times t$	0.0075	0.0025	0.0161	<0.0001	<0.0001	<0.0001
$I \times t$	0.9983	0.0639	0.4820	0.9553	0.9487	0.4615
$T \times I \times t$	0.9999	0.8965	0.3800	0.9836	0.9981	0.9905
Nitrate-N concentrations						
T	<0.0001	<0.0001	0.005	<0.0001	<0.0001	<0.0001
I	0.8290	0.7765	0.7685	0.8837	0.7109	0.5100
T	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
$T \times I$	0.9506	0.5422	0.5658	0.7468	0.7276	0.9868
$T \times t$	0.0009	<0.0001	0.2536	0.0299	<0.0001	0.0208
$I \times t$	0.9999	0.9527	0.9822	0.9763	0.8893	0.9970
$T \times I \times t$	1.0000	0.9875	0.9999	0.9960	0.9991	1.0000

Note: Probability values are significant at <0.05.

urea-N recovered, ΔNH_4^+-N concentration, and ΔNO_3^--N concentration with time for each soil. In this model, temperature and inhibitor treatment were fixed effects, replicate was a random effect, and time was the repeated factor. A covariance structure with the lowest AIC was used in the model statement. We used a three-way ANOVA in PROC GLIMMIX to determine the effect of temperature, soil, inhibitor treatment, and their interactions on the *k* and $t_{1/2}$ generated using a gamma distribution. Temperature, soil, and inhibitor treatment were fixed effects, whereas replicate and its interaction with fixed effects were random effects. Similarly, PROC GLIMMIX was used to compare the Q_{10}, E_a, ΔG, ΔH, and ΔS for the inhibitor treatments and soil. We used the SLICE statement in PROC GLIMMIX to request for mean separation by soils in all the GLIMMIX procedures. Means comparison was performed at a probability level of <0.05 Fisher's protected least significant difference (LSD).

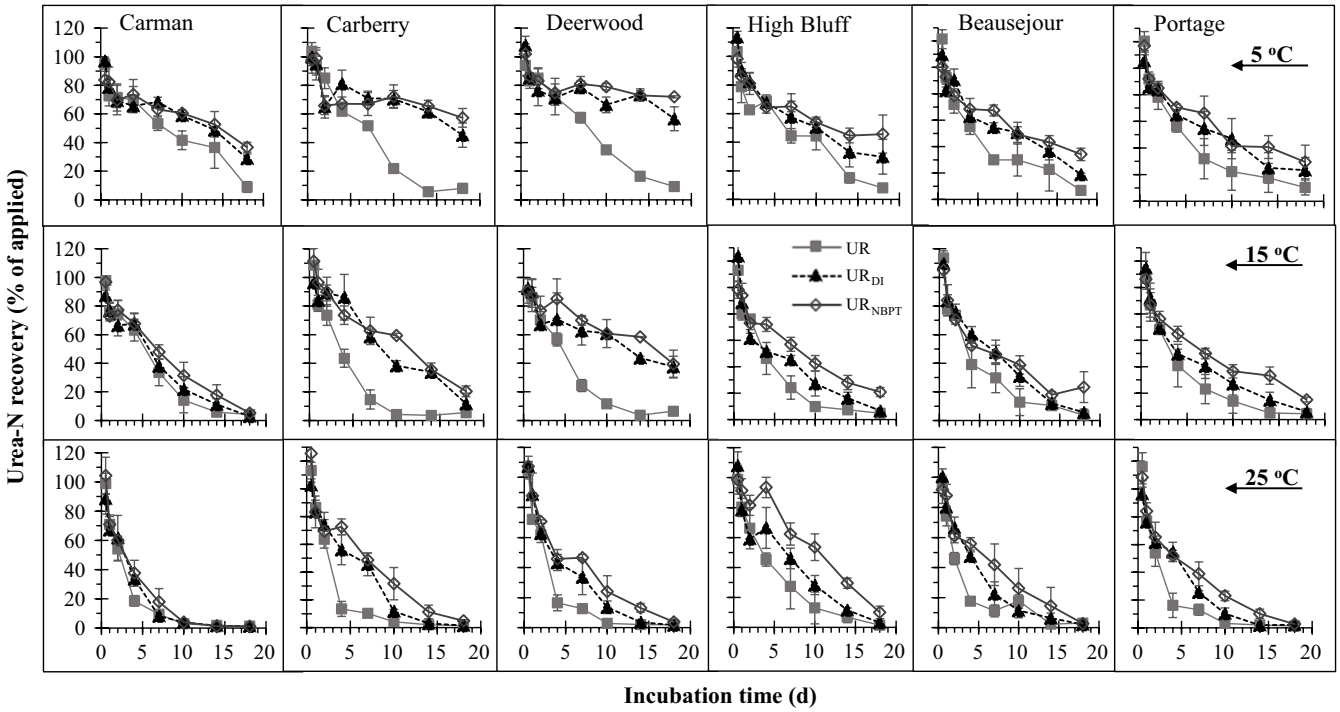
Results and Discussion

Effect of inhibitor treatment and temperature on urea-N recovery

There was no significant temperature × inhibitor treatment × time interaction in the amount of urea-N recovered in all soils except the neutral pH soils (CB and DW; Table 2). There was a significant inhibitor treatment × time interaction in the amount of urea-N recovered in all soils except CM (Table 2). The amount of urea-N recovered with time decreased with an increase in temperature for each inhibitor treatment. For example, less than 20% of applied urea-N in UR was recovered on 4 d in all soils (except DW soil) at 25 °C, whereas at least 40% of the applied urea-N was recovered in all the soils at 15 or 5 °C on 4 d. Low urea-N recovery with an increase in temperature in our study was because of the increase in urease activity at high temperatures as previously reported (Xu et al. 1993). As the temperature increased from 5 to 25 °C, the effectiveness of NBPT to increase urea-N recovery was smallest in CM soil (Fig. 1). As such, urea hydrolysis in CM soil was almost completed in all inhibitor treatments by 10 d at 25 °C (Fig. 1). The low effectiveness of NBPT at 25 °C in CM soil relative to other soils was because the efficacy of NBPT is lower in acidic than alkaline soils (Hendrickson and Douglass 1993) coupled with the increase in urea hydrolysis as a result of increased temperature. Similarly, results from a previous study that compared urea-N recovery at different soil pH (5.4, 7.8, and 8.1) found that urea treated with NBPT was completely hydrolyzed at 15 and 25 °C in acidic soil by 7 d when less than 40% of the applied urea had hydrolyzed in the alkaline soils (Suter et al. 2011).

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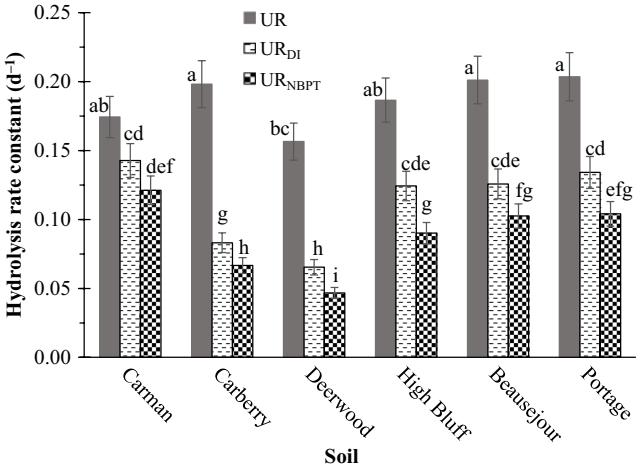
Fig. 1. Urea-N recovered (% of applied urea-N) in soils during an 18 d incubation period at 5, 15, and 25 °C. Error bars are standard errors of the mean. UR, untreated urea; UR_{DI}, urea treated with double inhibitor (combined NBPT and nitrification inhibitors); UR_{NBPT}, urea treated with NBPT.



Kinetics and thermodynamics of urea hydrolysis

There was no significant temperature × inhibitor treatment × soil interaction on k (Table 3). In addition, there was no significant interaction between temperature and soil nor between temperature and inhibitor treatment on k (Table 3). Averaged across soils and inhibitor treatments, k increased in the order of 0.07 d^{-1} at 5 °C, 0.12 d^{-1} at 15 °C, and 0.20 d^{-1} at 25 °C (a Q_{10} of approximately 2). There was no significant difference in Q_{10} between increasing the temperature from 5 to 15 °C and from 15 to 25 °C for each inhibitor treatment in each soil (results not shown). The significant increase in k with an increase in temperature was an indication that the soil urease activities increased with an increase in temperature as previously reported (Lei et al. 2018*a*). There was a significant effect of inhibitor treatment × soil interaction on k (Table 3). The significant inhibitor treatment × soil interaction was because when averaged across the three temperatures, k was greater in UR_{DI} than UR_{NBPT} in each of the soils except CM soil (Fig. 2). Overall, k was 38% greater in UR_{DI} than UR_{NBPT} across soil–temperature (Table 3). The greater k in UR_{DI} than UR_{NBPT} corroborated our previous study that compared k of the soils used in the study (except PP) at 21 °C and found k to be greater in UR_{DI} than UR_{NBPT} by 21% (Lasisi et al. 2020*b*). Although the percentage inhibition of k by NBPT was not dependent on temperature in UR_{NBPT}, the percentage inhibition of k was dependent on temperature in UR_{DI} across soils (Fig. 3).

Fig. 2. Interaction between soil and inhibitor treatments on urea hydrolysis rate constant. Error bars are standard errors of the mean. Bars with different letters within each soil are significantly different at a probability value of <0.05 Fisher's protected least significant difference. UR, untreated urea; UR_{DI}, urea treated with double inhibitor (combined NBPT and nitrification inhibitors); UR_{NBPT}, urea treated with NBPT.



The percentage inhibition of k by NBPT in UR_{DI} decreased by 25% as temperature increased from 5 to 25 °C. Although this present study did not include urea treated with NI as a treatment, previous studies that

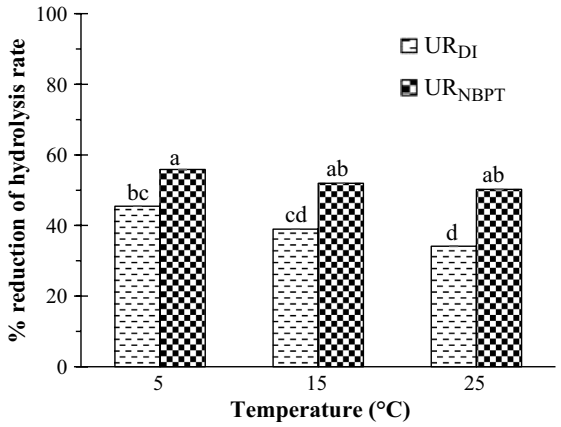
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Table 3. Effect of temperature, inhibitor treatment, and soil on urea hydrolysis rate constant (k) and half-life ($t_{1/2}$).

Model effect	k (d^{-1})	$t_{1/2}$ (d)
Temperature (T)		
5 °C	0.07c	10.0a
15 °C	0.12b	5.7b
25 °C	0.20a	3.5c
Inhibitor treatment (I)		
UR	0.19a	3.8c
UR_{DI}	0.11b	6.5b
UR_{NBPT}	0.08c	8.3c
Soil (S)		
Carman	0.15a	4.8c
Carberry	0.10b	6.8b
Deerwood	0.08c	9.0a
High Bluff	0.13a	5.5c
Beausejour	0.14a	5.1c
Portage	0.14a	4.9c
	Probability values	
T	<0.0001	<0.0001
I	<0.0001	<0.0001
S	<0.0001	<0.0001
$T \times I$	0.3286	0.2589
$T \times S$	0.4876	0.5041
$I \times S$	<0.0001	<0.0001
$T \times I \times S$	0.2925	0.2342

Note: UR, untreated urea; UR_{DI}, urea treated with double inhibitor (combined NBPT and nitrification inhibitors); UR_{NBPT}, urea treated with NBPT. Means with different letters within a column are significantly different at a probability value of <0.05 Fisher's protected least significant difference. Probability values are significant at <0.05.

Fig. 3. Percentage inhibition of urea hydrolysis rate by NBPT at 5, 15, and 25 °C across soils. Error bars are standard errors of the mean. Bars with different letters are significantly different at a probability value of <0.05 Fisher's protected least significant difference. UR, untreated urea; UR_{DI}, urea treated with double inhibitor (combined NBPT and nitrification inhibitors); UR_{NBPT}, urea treated with NBPT.



examined the impact of NI only on hydrolysis of urea have shown that NI did not interfere with the rate of urea hydrolysis in soils (Bremner and Bundy 1976; Ni et al. 2018).

The use of NBPT increased the half-life of urea by 8.2 d at 5 °C, 4.3 d at 15 °C, and 2.6 d at 25 °C across soils. However, the addition of NI with NBPT reduced the half-life of NBPT-treated urea by approximately 2 d across soil–temperature (Table 3). Previous studies (Soares et al. 2012; Frame 2017) have attributed the greater NH_3 volatilization from DI to the persistence of NH_4^+ by the NI. However, this study showed that the reduced half-life of NBPT-treated urea in the presence of NI may partly account for the increase in NH_3 volatilization from DI as previously reported in the literature (Gioacchini et al. 2002; Mariano et al. 2019). Although the mechanism for the interference of NI on NBPT inhibition effect is yet to be elucidated, we hypothesized that the presence of phosphoric acidic group on the NI (DMPP) created an acidic environment for the NBPT, which then has a potential of lowering the persistence of NBPT in soil (Engel et al. 2013).

The E_a, which is an indicator of the energy barrier that must be overcome for hydrolysis of urea to occur ranged from 20 to 54 $kJ \cdot mol^{-1}$ (Table 4). The values of E_a in our soils were within the range of 20–80 $kJ \cdot mol^{-1}$ reported in the literature (Gould et al. 1973; Kumar and Wagenet 1984; Moyo et al. 1989; Marshall et al. 1990; Lei et al. 2018*b*). Except in CM soils where ΔG was not different between UR and UR_{DI}, ΔG significantly increased in the order of $UR_{NBPT} > UR_{DI} > UR$ in each soil (Table 4). We found that ΔH and ΔS for each soil were not significantly different among the inhibitor treatments except in DW soil where UR had the smallest ΔH and ΔS among the inhibitor treatments (Table 4). The lack of significant difference in ΔH and ΔS between untreated urea and urea treated with inhibitor (UR_{DI} and UR_{NBPT}) corroborated the study of Juan et al. (2010) that reported that the use of NBPT had a greater impact on kinetics than thermodynamics of urea hydrolysis. Even when untreated urea at different application rates were used, Lei et al. (2018*b*) found that the interaction between urea application rates and temperature was significant on the kinetics of urea hydrolysis but not its thermodynamics parameters. As suggested by Moyo et al. (1989), the wide variations or differences in thermodynamic parameters among and within soils were due to other soil factors such as urea application rate, treatment type, and moisture that interact with temperature. The values of ΔG and ΔH being >0 and ΔS being <0 showed that the hydrolysis of urea in soil was endothermic and nonspontaneous. The lack of spontaneity of urea hydrolysis

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Table 4. Activation energy (E_a), change in Gibb's free energy (ΔG), enthalpy change (ΔH), and entropy change (ΔS) of the inhibitor treatments in each soil.

Soil	Inhibitor treatment	E_a (kJ·mol^{-1})	ΔG (kJ·mol^{-1})	ΔH (kJ·mol^{-1})	ΔS (J·mol^{-1}·K^{-1})
Carman	UR	48.9a	75.5b	41.1a	−116.4a
	UR_{DI}	54.4a	75.8b	51.6a	−81.4a
	UR_{NBPT}	53.8a	76.2a	48.8a	−92.6a
Carberry	UR	26.6b	75.7c	25.9a	−168a
	UR_{DI}	45a	77.4b	43.7a	−113.5a
	UR_{NBPT}	40.1a	78.1a	37.9a	−135.4a
Deerwood	UR	20.6c	76.5c	19.4b	−192.7b
	UR_{DI}	50.5a	77.9b	44.8a	−111.8a
	UR_{NBPT}	36.9b	79.0a	37.8ab	−138.7ab
High Bluff	UR	35.2a	75.7c	31.8a	−148.1a
	UR_{DI}	29.7a	76.8b	29.6a	−159.3a
	UR_{NBPT}	32.3a	77.5a	29.2a	−163.2a
Beausejour	UR	39.8a	75.4c	32.9a	−143.8a
	UR_{DI}	32ab	76.7b	28.7a	−162.1a
	UR_{NBPT}	25.1b	77.4a	24.1a	−179.9a
Portage	UR	29.8a	75.6c	25.9a	−168.1a
	UR_{DI}	27.3a	76.6b	26.8a	−168.4a
	UR_{NBPT}	29.1a	77.2a	26.3a	−172.1a

Note: UR, untreated urea; UR_{DI}, urea treated with double inhibitor (combined NBPT and nitrification inhibitors); UR_{NBPT}, urea treated with NBPT. Means with the same letters within a column for each soil are not significantly different at a probability value of <0.05 Fisher's protected least significant difference.

corroborated the results from an earlier study that found ΔG and ΔH of different rates of untreated urea to be >0 (Lei et al. 2018*b*).

Change in inorganic N concentrations

In the repeated measure ANOVA for ΔNH_4^+-N concentrations, there was no significant temperature × inhibitor treatment × time interaction in each of the soils (Table 2). Similarly, interaction between inhibitor treatment and time was not significant in each soil (Table 2). However, there was a significant temperature × time interaction in each soil. The ΔNH_4^+-N concentrations in each inhibitor treatment across soils increased with an increase in temperature and (or) time in the first 10 d (Fig. 4). At 25 °C, CM soil had a greater NH_4^+-N concentration than any other soils in each of the inhibitor reatments probably due to its greatest urea hydrolysis rate. On average across soil–temperature, NH_4^+-N concentrations were greater in UR than UR_{NBPT} in the first 10 d, which is an indication of greater k in UR than UR_{NBPT} (Fig. 4).

There was no significant temperature × inhibitor treatment × time interaction on NO_3^--N concentration in each of the soils (Table 2). In addition, interactions between inhibitor treatment × temperature and inhibitor treatment × time on NO_3^--N concentration were not significant in each soil (Table 2). The concentration of NO_3^--N in each soil increased as temperature increased (Fig. 5). Despite its fastest urea hydrolysis rate and greatest NH_4^+-N concentration, CM soil with acidic pH had lower NO_3^--N concentration than the alkaline soils. This may be due to the acidic pH of CM soil, which has the potential to reduce nitrification process when compared with alkaline soil pH (Ste-marie and Pare 1999; Yao et al. 2011). In addition, the ΔNO_3^--N accumulation increased as the sand content of the soils decreased in all the inhibitor treatments (Fig. 5). The decrease in ΔNO_3^--N accumulation with an increase in sand fraction of the soil in this study corroborated previous studies that reported lower NO_3^--N accumulation as sand faction of the soil increased (Goos and Guertal 2019; Lasisi et al. 2020*b*). Among the inhibitor treatments, the benefit of NI in reducing NO_3^--N accumulation in soil was not observed. The lack of the impact of NI may be compounded by the differences in the level of substrate availability (NH_4^+-N) for nitrification following urea hydrolysis. In addition, the relatively high urea concentration (and subsequent high NH_4^+-N concentration) within the fertilizer reaction zone may be toxic to nitrifying organisms as a result of a high osmotic pressure of the soil solution thereby resulting in reduced nitrification in all inhibitor treatments (Darrah et al. 1987; Harapiak et al. 1993). The steady increase in inorganic N concentration and decrease in urea-N recovered at 5 °C confirmed results from previous studies, which showed that N transformation could occur at temperatures typical of the fall season (Clark et al. 2009; Chantigny et al. 2019). The implication of this for Canadian prairie farmers is that N losses such as NH_3 volatilization could occur from surface-applied urea when the temperature is ≤5 °C (Lasisi et al. 2020*a*).

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Fig. 4. Change in ammonium-N concentrations during an 18 d incubation period at 5, 15, and 25 °C. Error bars are standard errors of the mean. UR, untreated urea; UR_{DI}, urea treated with double inhibitor (combined NBPT and nitrification inhibitors); UR_{NBPT}, urea treated with NBPT.

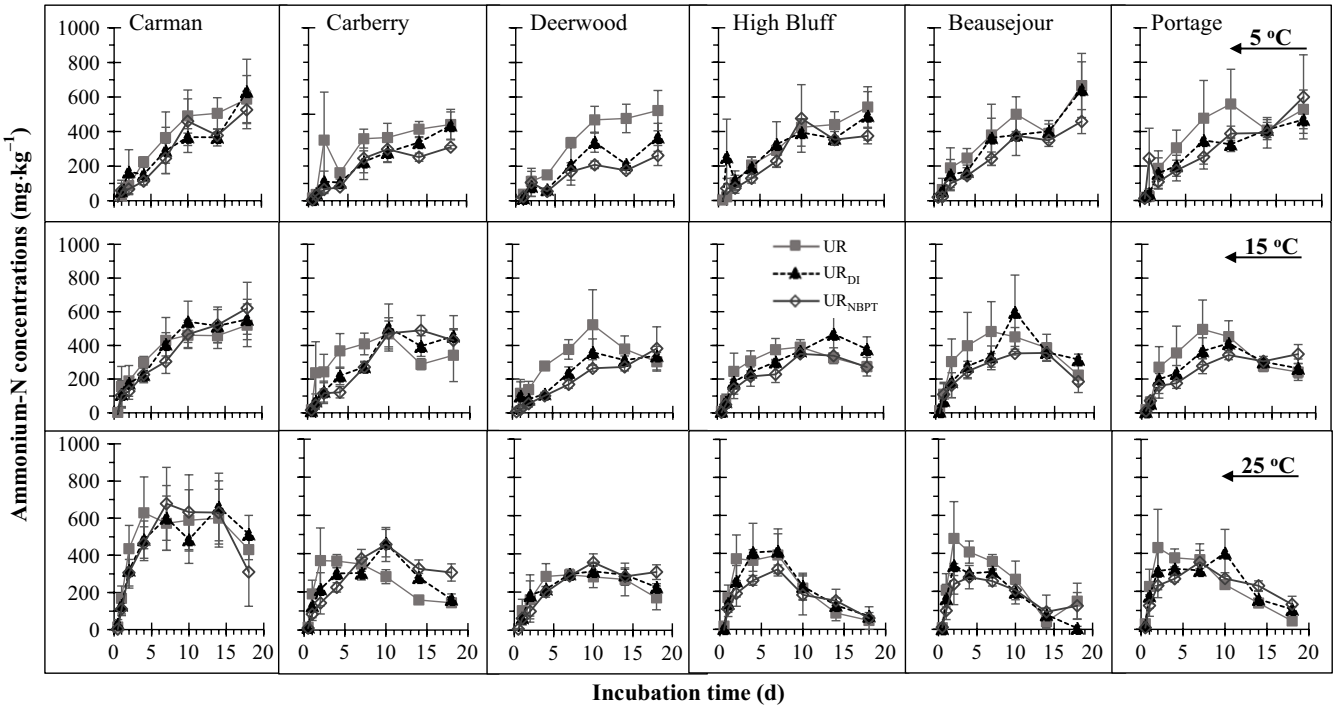
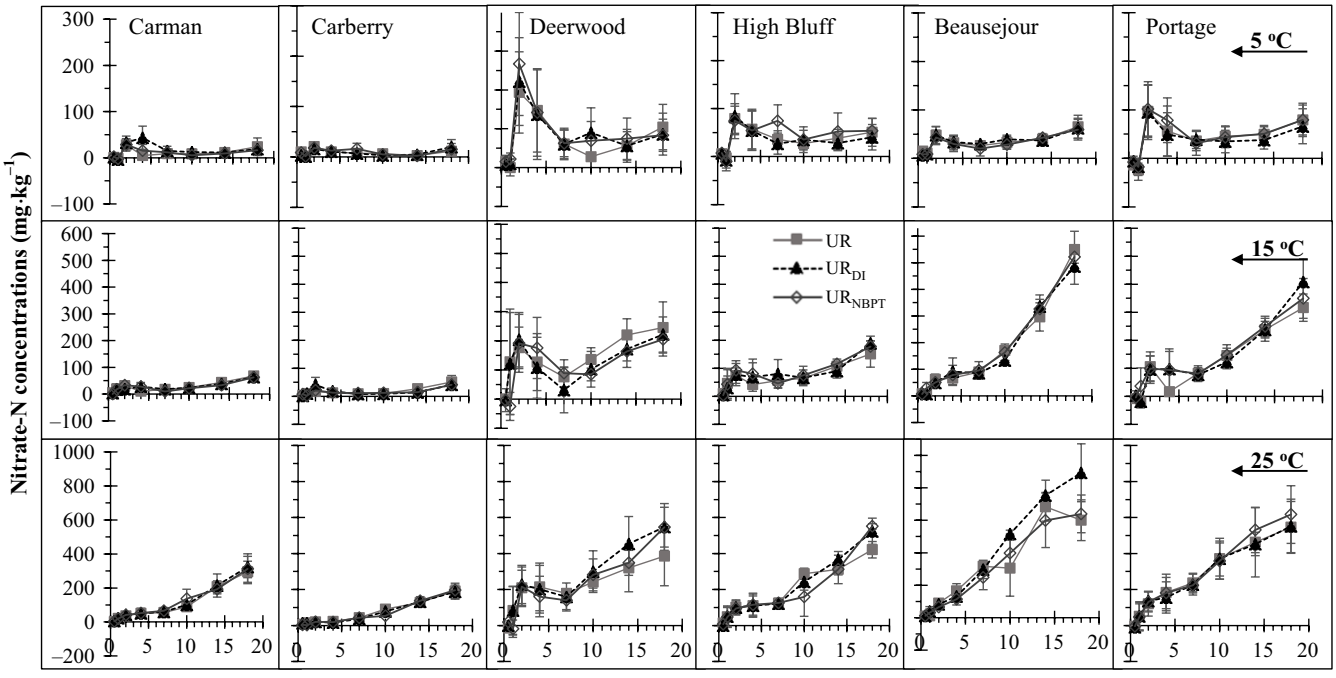


Fig. 5. Change in nitrate-N concentrations during an 18 d incubation period at 5, 15, and 25 °C. Error bars are standard errors of the mean. UR, untreated urea; UR_{DI}, urea treated with double inhibitor (combined NBPT and nitrification inhibitors); UR_{NBPT}, urea treated with NBPT. Note the differences in scale among temperatures.



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Conclusion

Our study demonstrated that urease inhibitor, NBPT, could reduce hydrolysis of urea at temperatures of 5, 15, and 25 °C across soils. The effectiveness of NBPT was greater in neutral to alkaline soils than in acidic soil. Our study showed that the addition of NI reduced the half-life of NBPT treated urea by approximately 2 d across soil–temperature. We found that percentage inhibition of urea hydrolysis by NBPT was independent of temperature but percentage inhibition by DI decreased by 25% as temperature increased from 5 to 25 °C across soils. Thermodynamic parameters showed that the hydrolysis of urea treated with and without NBPT or DI was nonspontaneous. The often-reported greater NH_3 volatilization from UR_{DI} than UR_{NBPT} may not only be due to the persistence of NH_4^+ by NI but also because NI reduced the inhibitory effect of NBPT on urea hydrolysis.

Acknowledgements

We would like to acknowledge the financial support of Active AgriScience Inc., BC and Natural Sciences and Engineering Research Council of Canada through the NSERC CRD grant. We recognize the contribution of Dr. Ranil Waliwitiya to the development of ARM U and ARM U Advanced. The technical support of Justin Soucie and the statistical advice of Dr. Zvomuya are well appreciated.

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