Effects of Combined Application of Nitrogen Fertilizer and Biochemical Inhibitors on Soil Potassium Leaching Characteristics in Yellow Clayey Paddy Soil (Postprint)

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Abstract

In the yellow mud paddy field soils of southern China, nutrient leaching is severe, particularly for nitrogen (N) and potassium (K), which not only causes resource waste and potential environmental threats but also severely restricts sustainable crop production. Using indoor soil column simulation incubation, this study investigated the effects of separately adding the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) and the nitrification inhibitor 2-chloro-6-(trichloromethyl) pyridine (CP) to urea (U) and urea ammonium nitrate (UAN), as well as their combined application, on potassium leaching characteristics in yellow mud paddy field soils, and explored fertilization techniques to improve potassium supply capacity. In leachates from different N fertilizer types, the average K+ concentration was higher in the UAN treatment (103.0 mg kg-1) than in the U treatment (93.9 mg kg-1), with significant differences observed among inhibitor treatments. At the end of incubation (day 72), K+ leaching loss in the UAN treatment was 6.7% higher than that in the U treatment. The cumulative K+ amount in leachates across U treatments followed the order: U > U+NBPT > U+NBPT+CP > U+CP > CK, with the U+NBPT, U+CP, and U+NBPT+CP treatments showing reductions of 8.7%, 20.2%, and 14.9% compared to the U treatment, respectively. Across UAN treatments, the cumulative K+ amount in leachates followed the order: UAN > UAN+NBPT > UAN+NBPT+CP > UAN+CP > CK, with the UAN+NBPT, UAN+CP, and UAN+NBPT+CP treatments reducing by 6.0%, 13.8%, and 9.2% compared to the UAN treatment, respectively. The K+ leaching rates across different fertilization treatments followed the order: UAN > UAN+NBPT > U > UAN+NBPT+CP > UAN+CP > U+NBPT > U+NBPT+CP > U+CP. At mid-incubation (day 36), soil available K content in fertilizer microsites of U and UAN treatments decreased significantly, whereas CP-added treatments effectively maintained higher soil available K content. Compared with sole NBPT application, combined CP application reduced NO3- leaching in yellow mud paddy field soils, increased K+ fixation by soil lattices, and mitigated K+ leaching risk, with an effective duration exceeding 72 days. The relationship between cumulative K+ amount (y) and cumulative NO3- amount (x) in leachates across treatments was fitted, with the linear equation (y=ax+b) and Elovich equation (y=alnx+b) showing the highest goodness of fit, and significant differences in a and b values were observed among inhibitor treatments. In conclusion, sole CP application or combined application with NBPT in yellow mud paddy field soils can effectively increase K+ adsorption, reduce soil K+ leaching loss, mitigate nutrient leaching risk, and improve fertilizer use efficiency.

Full Text

Effects of Nitrogen Fertilization Combined with Biochemical Inhibitors on Leaching Characteristics of Soil Potassium in Yellow Clayey Soil

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Abstract

Soil nutrient leaching in yellow clayey soil, particularly nitrogen (N) and potassium (K), is extremely serious in southern China, resulting not only in resource waste and potential environmental threats but also severely restricting sustainable crop production. This study investigated the effects of a urease inhibitor (N-(n-butyl) thiophosphoric triamide, NBPT), a nitrification inhibitor (2-chloro-6-(trichloromethyl) pyridine, CP), and their combined application on K leaching characteristics in yellow clayey soil using an indoor soil column simulation with urea (U) and urea ammonium nitrate (UAN). In leachate from different N fertilizers, the average K concentration was higher in UAN treatment (103.0 mg/kg) than in U treatment (93.9 mg/kg), with significant differences among inhibitor treatments. At the end of incubation (Day 72), UAN treatment increased K leaching amount by 6.7% compared to U treatment. K accumulation in leachate among U treatments followed the order: U > U+NBPT > U+NBPT+CP > U+CP > CK. Compared with U treatment, K accumulation was reduced by 8.7%, 20.2%, and 14.9% in U+NBPT, U+CP, and U+NBPT+CP treatments, respectively. Among UAN treatments, K accumulation followed: UAN > UAN+NBPT > UAN+NBPT+CP > UAN+CP > CK, with reductions of 6.0%, 13.8%, and 9.2% compared to UAN treatment. The K leaching rate across treatments ranked: UAN > UAN+NBPT > U > UAN+NBPT+CP > UAN+CP > U+NBPT > U+NBPT+CP > U+CP. At mid-incubation (Day 36), soil available K content in fertilizer microsites decreased significantly in U and UAN treatments, while CP addition effectively maintained high available K content in topsoil. Compared with NBPT alone, combined CP application reduced NO leaching, increased K fixation by soil lattice, and mitigated K leaching risk for over 72 days in yellow clayey soil. Equation models describing the relationship between K accumulation (y) and NO accumulation (x) in leachate showed that linear ($y = ax+b$) and Elovich ($y = a\ln x+b$) equations fit best, with significant differences in a and b values among inhibitor treatments. In conclusion, CP application alone or combined with NBPT in yellow clayey soil can effectively increase K adsorption, minimize soil K leaching loss, mitigate nutrient leaching risk, and improve fertilizer utilization efficiency.

Keywords: K ; Yellow clayey soil; Urease inhibitor; Nitrification inhibitor; N-(n-butyl) thiophosphoric triamide (NBPT); 2-chloro-6-(trichloromethyl) pyridine (CP); Urea; Urea ammonium nitrate; Leaching

Potassium (K) is an essential macronutrient for plant growth and development, playing a vital role in metabolic processes [1-2]. Soil K deficiency can cause crop yield losses due to physiological disorders [3], and K fertilizer application represents an important approach to alleviate K deficiency [4]. Currently, China has become a major K fertilizer consumer worldwide [5], yet K fertilizer resources are scarce [6], with import volume ranking first globally [7].

Yellow clayey soil belongs to the percolating paddy soil subgroup and represents one of the important low- and medium-yield paddy fields in southern China [8], covering approximately 1.4 million hectares. These soils are primarily distributed on hilly slopes, characterized by shallow plow layers, heavy texture, and low maturity [9]. The parent materials are weathered products of acidic crystalline rocks and sandstone, along with some Quaternary red clay. Due to moderate weathering and intensive leaching, these soils are acidic to strongly acidic (pH 4.5-5.5) with low exchangeable base content and base saturation <35% in the B horizon [10]. Consequently, yellow clayey soils have low available nutrient content, poor fertility, and weak nutrient retention capacity, making them prone to substantial nutrient losses from indiscriminate fertilization [11], with K deficiency being particularly severe [12].

Soil properties affecting K leaching primarily include pH [13], soil mineral type [14], exchangeable K content [15], and texture [16]. Research indicates that in acidic soils, aluminum and hydroxy-aluminum ions can occupy K selective binding sites, inhibiting K adsorption by soil minerals and leaving most K in soil solution, thereby exacerbating leaching [17-18]. NH and K have similar ionic radii and compete for soil adsorption sites, so N fertilizer application inevitably affects K adsorption [13]. Ma et al. [19] found that urea application promoted K loss in red soils. Du et al. [20-21] reported that combined ammonium-potassium fertilizer application significantly increased water-soluble K content in fertilizer microsites while reducing K fixation by soil lattice.

Studies have shown that nitrification inhibitors significantly reduce soil nitrate leaching, and according to the principle of solution charge balance, leaching losses of some soil cations such as K , Ca^{2} , and Mg^{2} are correspondingly reduced [22-24]. Meanwhile, urease inhibitors can inhibit soil urease activity and slow the hydrolysis of urea-N to NH -N [25]. Currently, research on the effects of different N fertilizer types on nutrient leaching characteristics in southern acidic soils is limited and primarily focuses on N. No studies have reported on the effects of combined inhibitor application on K leaching characteristics. Therefore, this study employed indoor simulation experiments to investigate the effects of different N fertilizer types combined with various inhibitor combinations on K leaching characteristics in yellow clayey soil, aiming to provide a scientific basis for optimized fertilization management in low- and medium-yield fields.

1.1 Experimental Materials

The test soil was yellow clayey paddy soil developed from Quaternary red soil, collected from the 0-20 cm plow layer in Jinzhu Village, Langya Town, Wucheng District, Jinhua City, Zhejiang Province (29°01’ 19” N, 119°27’ 96” E) in October 2013. The region is located on the eastern edge of the Jinqu Basin with a mid-subtropical monsoon climate, 86 m altitude, average annual rainfall of 1,424 mm, and average annual temperature of 17.5°C. Fresh soil samples were cleaned of debris and roots, air-dried, and passed through a 2 mm sieve. Basic physicochemical properties were: pH(H O) 5.24 (soil:water = 1:1), CEC 7.32 cmol · kg^{1}, organic matter 26.20 g · kg^{1}, total N 1.25 g · kg^{1}, alkaline-hydrolyzable N 132.30 mg · kg^{1}, NH -N 17.81 mg · kg^{1}, NO -N 53.40 mg · kg^{1}, available P 4.43 mg · kg^{1}, available K 79.00 mg · kg^{1}, sand 32.82%, silt 44.13%, and clay 23.05%.

Urea (46% N), calcium superphosphate (12% P O), and potassium chloride (60% K O) were analytical grade reagents from Sinopharm Chemical Reagent Co., Ltd. Urea ammonium nitrate (32% N) was analytical grade from Sinochem Crop Nutrition Co., Ltd. The urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) and nitrification inhibitor 2-chloro-6-(trichloromethyl) pyridine (CP, 24% emulsifiable concentrate) were analytical grade from Zhejiang Aofutuo Chemical Co., Ltd.

1.2 Experimental Setup

The simulated soil column apparatus consisted of PVC cylinders (10 cm inner diameter, 40 cm height) [26]. A 2 cm layer of dried quartz sand (1-2 mm particle size) was placed at the bottom, with a 2 cm hole connected to plastic tubing for leachate collection. A 200-mesh nylon filter cloth was placed at the bottom and at the sand-soil interface. Air-dried soil was packed into the PVC columns at a bulk density of 1.25 g · cm^{3} to form a soil column approximately 30 cm high.

1.3 Experimental Design

The experiment was conducted from April to June 2015 in a laboratory at Zijingang Campus, Zhejiang University, Hangzhou, with indoor temperature maintained at 25-35°C and no crops planted. The experiment comprised two groups, each with nine treatments and three replicates, as shown in Table 1 . Soil was packed in two layers (0-10 cm and 10-30 cm from top to bottom). Urea/urea ammonium nitrate and biochemical inhibitors were mixed uniformly with calcium superphosphate and potassium chloride, then thoroughly mixed with the 0-10 cm soil layer before being applied to the soil surface. N application rate was 300 kg · hm ^{2}, with P O and K O both at 150 kg · hm ^{2}.

1.4 Sample Collection and Analysis

1.4.1 Sample Collection After column installation, 200 mL of water was slowly injected daily from the top using a syringe (equivalent to local average rainfall of 25.5 mm) [26]. To approximate natural precipitation, intermittent leaching was employed to allow soil reaction time. Simulated rainfall began on Day 6 when leachate started flowing, applied every 6 days at 200 mL per event. Leachate was collected 12 times total on Days 1, 6, 12, 18, 24, 30, 36, 48, 54, 60, 66, and 72. On Days 36 and 72, soil columns were destructively sampled in six layers (0-5, 5-10, 10-15, 15-20, 20-25, and 25-30 cm) to determine the dynamic distribution of available K content across the soil profile.

1.4.2 Measurement Items and Methods Basic soil physicochemical properties were determined using conventional methods [27]. After each leachate collection, samples were thoroughly mixed and volume measured. K concentration was determined by flame photometry, and NO -N concentration by UV spectrophotometry. Cumulative leaching volume was calculated by summing each leaching event. For stratified soil samples, K concentration in extracts was immediately determined by flame photometry after extraction with 1 mol/L NH OAc.

1.4.3 Calculation Formula K leaching rate (%) = (K cumulative leaching amount in N-treated soil -K cumulative leaching amount in CK) / K application rate × 100% [29-30] (1)

1.5 Data Analysis

Statistical analysis was performed using Excel 2003 and SPSS 17.0 software, with Duncan's new multiple range test used for comparing significant differences among treatments.

2 Results and Analysis

2.1 K Concentration in Leachate Under Different Treatments

As shown in Figure 1 [Figure 1: see original paper], K concentrations in leachate remained relatively stable throughout the incubation period, ranging from 55.8-92.0 mg • kg^{1} in CK, 62.0-112.3 mg • kg^{1} in U treatments, and 71.5-137.5 mg • kg^{1} in UAN treatments. Average K concentrations were higher in UAN (103.0 mg • kg^{1}) than in U (93.9 mg • kg^{1}), with significant differences among inhibitor treatments. During early incubation (Day 18), K concentrations (mg • kg^{1}) ranked as U (104.3) > CK (84.5) > U+NBPT (82.8) > U+NBPT+CP (70.5) > U+CP (66.8) for U treatments, and UAN (124.5) > UAN+NBPT (86.8) > UAN+NBPT+CP (86.5) > CK (84.5) > UAN+CP (82.5) for UAN treatments. These results indicate that different N fertilizer types exacerbated K leaching, particularly UAN treatment, while inhibitor addition effectively mitigated K leaching risk, with CP showing better efficacy.

2.2 Cumulative K Leaching Under Different Treatments

As shown in Figure 2 [Figure 2: see original paper], cumulative K leaching increased progressively over time, with treatment differences becoming more pronounced. At mid-incubation (Day 36), UAN treatment increased cumulative K leaching by 9.9% compared to U treatment. For U treatments, cumulative K leaching ranked: U > U+NBPT > U+NBPT+CP > U+CP > CK, with reductions of 12.5%, 22.3%, and 22.7% in U+NBPT, U+CP, and U+NBPT+CP treatments, respectively. For UAN treatments, the order was UAN > UAN+NBPT+CP > UAN+CP > UAN+NBPT > CK, with reductions of 15.20%, 15.17%, and 12.54% compared to UAN.

At the end of incubation (Day 72), UAN treatment increased cumulative K leaching by 6.7% compared to U treatment. Cumulative K leaching ranked: U > U+NBPT > U+NBPT+CP > U+CP > CK for U treatments (reductions of 8.7%, 20.2%, and 14.9%), and UAN > UAN+NBPT > UAN+NBPT+CP > UAN+CP > CK for UAN treatments (reductions of 6.0%, 13.8%, and 9.2%). These results demonstrate that CP and NBPT effectively reduced K leaching losses in yellow clayey soil, with CP showing better efficacy in U treatments, possibly related to urea hydrolysis processes and N form transformations.

2.3 K Leaching Rate Under Different Treatments

As shown in Figure 3 [Figure 3: see original paper], at the end of incubation (Day 72), UAN treatment had a 26.7% higher K leaching rate (13.67%) than U treatment (10.79%). For U treatments, K leaching rates ranked: U > U+NBPT > U+NBPT+CP > U+CP, with significant reductions of 34.6% ($P<0.05$), 80.6% ($P<0.05$), and 59.7% ($P<0.05$) in U+NBPT, U+CP, and U+NBPT+CP treatments, respectively. For UAN treatments, the order was UAN > UAN+NBPT > UAN+NBPT+CP > UAN+CP, with reductions of 20.1%, 46.3% ($P<0.05$), and 31.0% ($P<0.05$), respectively. These results confirm that CP and NBPT significantly reduced K leaching losses after fertilization in yellow clayey soil, with CP showing better efficacy in U treatments.

2.4 Fitting of K and NO Leaching Characteristic Curves

As shown in Figure 4 [Figure 4: see original paper], NO cumulative leaching in soil columns increased steadily without major fluctuations. CK treatment remained at low levels throughout, while U and UAN treatments showed gradual increases initially, then sharp increases starting on Days 42 and 24, respectively. Regression analysis was performed on the relationship between K cumulative leaching (y) and NO cumulative leaching (x) using equations y = ax+b, y = alnx+b, y = ax , and lny = ax+b (Table 2). All equations showed highly significant R^2 values ($P<0.01$), indicating K leaching increased with NO leaching. Linear equation y = ax+b best described the relationship for both U and UAN treatments, effectively representing the rate of K leaching change with NO . For U treatments, a values ranked: U < U+NBPT < U+NBPT+CP < U+CP; for UAN treatments: UAN < UAN+NBPT < UAN+NBPT+CP < UAN+CP. Parameter b represents initial K leaching amount, ranking as U > U+NBPT > U+NBPT+CP > U+CP for U treatments, and UAN > UAN+NBPT > UAN+NBPT+CP > UAN+CP for UAN treatments. These results demonstrate that K leaching is closely related to NO leaching, and inhibitor addition can maintain N forms in soil and alter NO leaching dynamics. Parameter a represents the rate of K leaching with NO leaching.

2.5 Soil Profile Distribution of Available K

As shown in Figure 5 [Figure 5: see original paper], available K content in fertilizer microsites of yellow clayey soil decreased gradually with distance from the fertilization point across the 0-30 cm profile, with rapid K migration in the surface layer (0-10 cm). Both U and UAN treatments promoted K vertical migration compared to CK.

At mid-incubation (Day 36), U treatment had 9.20% higher available K content than UAN treatment in the 0-5 cm layer. For U treatments, available K content in 0-5 cm ranked: U+CP > U+NBPT+CP > U+NBPT > U, with increases of 1.96%, 35.01%, and 6.17% in U+NBPT, U+CP, and U+NBPT+CP treatments, respectively. For UAN treatments, the order was UAN+CP > UAN+NBPT > UAN+NBPT+CP > UAN, with increases of 27.14%, 28.67%, and 24.66%, respectively. These results indicate that CP and NBPT addition can maintain higher available K content in yellow clayey soil, with better efficacy in U treatments, possibly related to urea hydrolysis time.

3 Discussion

3.1 Effects of N Fertilizer Types on Soil K Leaching

Lin et al. [31] found that N fertilizer types affected base cation leaching in latosol in the order: ammonium sulfate > ammonium nitrate > urea. Luo et al. [30] reported that K concentration and cumulative leaching in latosol leachate ranked: compound fertilizer b > ammonium bicarbonate urea > compound fertilizer a. Yu et al. [28] found total base cation leaching (kg · hm ^{2}) ranked: ammonium sulfate (1821.12) > ammonium nitrate (1080.27) > urea (872.24) > N0 (417.23), with migration rates following: ammonium sulfate (26.28%) > ammonium nitrate (13.37%) > urea (11.78%). Our results align with previous studies [28], showing significant effects of N fertilizer types on K leaching characteristics in yellow clayey soil. Higher average K concentrations and leaching rates in UAN than U treatment at the end of incubation indicate that K leaching characteristics are related to N forms in fertilizers. Each mole of NH -N produces more H than urea when applied to soil, and more H replaces more base cations from soil colloids [28]. UAN contains mostly NH -N and NO -N, which interact more directly with soil than urea. During the first 18 days, K leaching increased slowly with minimal treatment differences. Subsequently, cumulative K leaching increased rapidly with steeper curve slopes and faster leaching rates (Figure 2 [Figure 2: see original paper]), related to urea hydrolysis processes [25] where urea is hydrolyzed to NH -N then nitrified to NO -N, requiring time.

3.2 Effects of Inhibitors on Soil K Leaching

NH -N is not easily adsorbed by soil colloids and is highly mobile, becoming the main form of N leaching loss, though less intense than NO -N leaching. However, soil colloid cation adsorption capacity is limited, and when fertilizer rates exceed adsorption capacity, NH leaching occurs [31, 36]. NH and K have nearly identical ionic radii and hydration energies, competing for fixation sites in clay mineral lattices and potentially altering K fixation and release characteristics [37]. Di et al. [38-39] found that nitrification inhibitors reduced cation leaching (K , Ca^{2} , Mg^{2}) in grassland soils, with NO concentration linearly related to total cations. Our results show that inhibitor addition effectively maintained higher available K content, slowed K downward migration, and improved surface soil K availability, while reducing NO leaching with synergistic effects when combined [25]. K leaching rates ranked: UAN > UAN+NBPT > U > UAN+NBPT+CP > UAN+CP > U+NBPT > U+NBPT+CP > U+CP. CP addition effectively reduced K concentration and cumulative leaching, while NBPT had smaller effects than CP. Under certain fertilizer rates, single CP application or combined with NBPT significantly reduced K leaching and mitigated nutrient loss risk in yellow clayey soil.

3.3 K Leaching Characteristics in Yellow Clayey Soil

Research indicates that N fertilizer rate, rainfall, temperature, and soil properties all affect K movement and leaching [13, 32]. Zhan et al. [33] reported that higher soil clay content increases K retention, with blocking factors showing highly significant linear relationships with clay content in each horizon. Acidic soils are highly weathered leached soils with high clay content; K adsorbed or fixed by soil particles is more exchangeable during initial leaching stages [34], but as fertilization and leaching continue, H accumulation breaks soil electrochemical equilibrium, drastically reducing K binding energy with decreasing pH and intensifying K release in later leaching stages [28]. Du et al. [20] found that NH in soil gradually decreased with incubation time, increasing H production and enhancing K exchange capacity. Lin et al. [35] reported that base cation leaching increased with NO leaching, showing good coupling between NO leaching and base cations, with migration rates ranking: ammonium sulfate > ammonium nitrate > urea. Southern yellow clayey soils are characterized by low maturity, organic matter deficiency, low available P and K, strong acidity, and poor tilth [40-41]. Under surplus conditions, red paddy soils dominated by non-swelling kaolinite minerals have low K fixation capacity [40], making it difficult for increased water-soluble or exchangeable K to enter mineral interlayers for fixation. Our results show that U and UAN treatments significantly reduced available K content in fertilizer microsites, decreasing K fixation by soil lattice. The presence of H and NO leaching reduced the K adsorption ratio, increasing leaching risk. Soil K leaching exhibits coupled migration characteristics with NO leaching.

Under our experimental conditions, K leaching rates ranked: UAN > UAN+NBPT > U > UAN+NBPT+CP > UAN+CP > U+NBPT > U+NBPT+CP > U+CP. Changes in K cumulative leaching (y) with NO cumulative leaching (x) in different N fertilizer treatments could be described by both linear and Elovich equations. Single CP application or combined with NBPT in yellow clayey soil can effectively increase K adsorption, reduce K leaching loss, mitigate nutrient leaching risk, and improve fertilizer utilization efficiency. However, these results were obtained under indoor simulation conditions without crop nutrient uptake; the actual field application effects of NBPT+CP combinations in yellow clayey soil require further investigation.

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