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Ammonium fractions and their kinetic release in salt-affected soils, Northeast Thailand

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Abstract

Importance of the work: Release and fractions of ammonium (NH_4^+-N) as differently influenced by salinity and sodicity are crucial for jasmine rice production.

Objectives: To investigate NH_4^+-N fractions and their kinetic release in salt-affected soils with different salinity and sodicity levels.

Materials and Methods: The soil N status was studied in seven salt-affected soils using the chemical sequential fractionation of soil NH_4^+-N and the kinetics of NH_4^+-N release based on successive extractions with 0.01 M $CaCl_2$ solution. In addition, spiked soil samples with the addition of 1,000 mg NH_4^+/kg were prepared for the kinetic release of recently fixed NH_4^+-N.

Results: The non-exchangeable NH_4^+-N fraction was dominant in the tested native soils, accounting for 60.5–89.0% of the total concentration, while the exchangeable and water-soluble NH_4^+-N fractions were similarly lower (1.71–14.86 and 1.29–9.65 mg/kg, respectively). The NH_4^+-N release was in the range 6.2–20.3% of the total N in the soils. When NH_4^+-N was added, 10.9–36.7% of the NH_4^+-N was fixed. The kinetics of NH_4^+-N release for both the native and the spiked soil samples were biphasic and best described using Elovich models. The release rate constants of NH_4^+-N were positively governed by the total N, organic matter, silt and the exchangeable and non-exchangeable NH_4^+-N contents. In contrast, soil pH and all sodicity-related parameters had strongly negative correlations with the NH^+_4 release rate, with exchangeable Na having the highest correlation among the sodicity-related parameters. On the other hand, salinity was not correlated with the NH_4^+-N release rate.

Main finding: Sodicity, particularly exchangeable Na, appeared more responsible than salinity for the low rate of NH_4^+-N release in these salt-affected soils.

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Introduction

Salt-affected soils occupy roughly 20% of land globally and pose a serious threat to agriculture, being problematic in over 120 countries (Rengasamy, 2010; Ivushkin et al., 2019), including Thailand, where these soils were reported to account for 1.84 million ha that generally support lowland rice cultivation (Arunin and Pongwichian, 2015). Soil nitrogen (N), one of the essential plant nutrients, is both a key soil quality factor and among the most important nutrient inputs to soils under agricultural production (Fageria, 2014; Fageria and Baligar, 2001). It is a cmmon knowledge that the main N source in soils for plants results from the mineralization of soil organic matter (SOM) (Curtin and Wen, 1999). The role of N becomes more important in salt-affected soils where biological activity is poor; hence, any possibility of N addition through biological fixation is meager (Bernhard et al., 2007; Duan et al., 2018). Insufficient N becomes a crucial problem when crops are grown in such soils (Abdelgadir et al., 2005); consequently, the application of fertilizers containing NH^+_4 is a common practice to increase crop growth and yield.

The primary available form of soil-based N for crops is ammonium (NH_4^+-N) which is converted to nitrate (NO^-_3-N), another available form, through the nitrification process under aerobic conditions (Zeng et al., 2016). On the other hand, NH_4^+ can be the ion adsorbed at the exchange site of colloids (referred to as exchangeable NH_4^+-N) and adsorbed by clay particles (referred to as fixed NH_4^+-N or non-exchangeable NH_4^+-N). Under favorable conditions (Feigenbaum et al., 1994; Nieder et al., 2011), NH_4^+-N is subsequently released into the soil solution and nitrified into NO^-_3-N. However, in salt-affected soil, nitrification is inhibited due to the adverse impact of salinity and sodicity on nitrifying microorganisms (Moussa et al., 2006; Bernhard et al., 2007; Sahrawat, 2008). Ammonium that has originated from applied fertilizers is fixed in the interlayer of clay minerals (Nieder et al., 2011). The fixed NH_4^+ ions are released due to the drive from a large concentration gradient between external NH_4^+-N in the soil solution and the interlayer-fixed NH_4^+ (Tang et al., 2008; Lu et al., 2010). Furthermore, NH_4^+ can be fixed during the genesis of clay minerals (defined as native fixed), which is normally trapped more in the center of the interlayers in the clay mineral structure (Steffens and Sparks, 1997), being an important reservoir of N in soils, due to it release providing NH_4^+-N when the level of NH_4^+-N in the soil solution is low. Therefore, the fixation and kinetic release of NH_4^+-N by soils are major processes in N transformation and in increasing a soil's ability to retain soil N fertility (Zhang et al., 2007), as well as in determining the efficiency of N fertilizers through the protection of soil N supplies against leaching (Nieder et al., 2011).

On the other hand, greater NH_4^+-N accumulation at increased salinity levels has been attributed to the inhibitory effect of toxic ions (particularly sodium, chloride and sulfate) on specific microbial functions during nitrification (Irshad et al., 2005; Lodhi et al., 2009; Akhtar et al., 2012). However, the fate of released fixed NH_4^+-N, likely converted to organic N or NO^-_3-N, depends on the competitive equilibrium between heterotrophic microorganisms and autotrophic-nitrifying bacteria, although both biological processes promote the release of fixed NH_4^+-N via the consumption of NH_4^+-N (Xiao et al., 2020). In addition, there are many N transformation pathways in the soil, including the release kinetics of fixed NH_4^+-N, which play a vital role in promoting soil N supply in agriculture. The release of fixed NH_4^+-N is related to many factors, such as clay mineral composition, exchangeable potassium and NH_4^+-N concentrations in the soil solution (Beauchamp, 1982; Nieder et al., 2011; Scherer et al., 2014). It has been reported that salinity and sodium were presumed to play an important role in NH_4^+-N availability (Laura, 1977; Irshad et al., 2005; Wichern et al., 2006 Duan et al., 2018); however, there are no known published studies carried out in lowland humid salt-affected soils such as in Northeast Thailand. Therefore, the current research aimed to determine the variations in the NH_4^+-N fractions and to investigate the release behavior of NH_4^+-N in relation to various factors, including newly added NH_4^+-N that can be fixed in salt-affected soils with different levels of salinity and sodicity.

Materials and Methods

Soil samples

The seven representative, salt-affected areas used in this study were identified and samples were taken from the paddy rice fields of several farmers in the Khorat basin, Northeast Thailand (Table 1). At each site, the ploughed layer (0–20 cm) of soil was sampled in July 2019 before rice transplantation. Each sample was air-dried and ground to pass through a 2 mm sieve in preparation for subsequent analyses.

Table 1 Soil classification unit, salt-affected soil diagnostic and mineralogical composition of studied soils collected from ploughed layer (0–20 cm)

Soil series (abbreviations used in text)	Coordinates	Soil classification	Salt-affected soil diagnostic	ECe (dS/m)	SAR	ESP (%)	Clay mineralogy^4
Phimai (Pm1)	15°14'11.4"N, 102°28'54.3"E	Typic Natraquert	Sodic	1.5 (0.19)	7.6 (0.22)	16.0 (2.04)	Sm, Ill, Kao
Phimai (Pm2)	15°14'48.0"N, 102°23'29.1"E	Typic Natraqualf	Saline-sodic	25.2 (0.80)	26.9 (0.14)	79.3 (1.99)	Sm, Ill, Kao
Kula Ronghai (Ki1)	15°11'13.5"N, 102°20'39.2"E	Typic Natraqualf	Saline-sodic	10.8 (0.38)	51.3 (1.57)	71.7 (3.44)	Kao, Ill, Quz
Kula Ronghai (Ki2)	15°24'09.0"N, 103°22'45.7"E	Typic Natraqualf	Saline-sodic	5.0 (0.90)	15.8 (0.68)	23.3 (2.83)	Kao, Ver, Ill, Quz
Roi-Et (Re1)	15°07'18.8"N, 101°54'50.8"E	Typic Natraqualf	Saline-sodic	36.3 (2.84)	37.5 (1.41)	210.4 (6.33)	Kao, Quz
Roi-Et (Re2)	15°28'56.3"N, 103°37'05.1"E	Typic Natraqualf	Saline-sodic	14.0 (0.18)	6.2 (0.63)	56.4 (5.34)	Kao, Quz
Udon (Ud)	15°12'09.5"N, 102°03'30.0"E	Typic Halaquept	Saline-sodic	10.6 (1.51)	85.4 (0.99)	148.9 (3.35)	Kao, Quz, Ill,

ECe = electrical conductivity of saturated paste extract; SAR = sodium adsorption ratio; ESP = exchangeable sodium percentage; Sm = smectite, Kao = kaolinite, Ver = vermiculite, Ill = illite, Quz = quartz (reported in descending order).
Values are presented as mean (± SD) from three replicates.

Physicochemical of salt-affected soils used in this study

The basic physicochemical properties of the soils were measured using standard methods. The soil texture was analyzed using the pipette method (Gee and Bauder, 1986). The soil pH was analyzed in a soil-to-water ratio of 1:1 using a glass electrode pH meter (National Soil Survey Center, 2004). The soil organic matter content was determined using the Walkley and Black titration method (Nelson and Sommers, 1996). Exchangeable cations (Na, K, Mg and Ca) of the soil were extracted with 1 M ammonium acetate (NH_4OAc) at pH 7.0 and were quantified using atomic absorption spectrophotometry (AAS), according to Thomas (1996). Cation exchange capacity (CEC) was determined using 1 M NH_4OAc following the procedure of Chapman (1965). The exchangeable sodium percentage (ESP) was defined as the ratio of exchangeable Na to the CEC of the soil (Richards, 1954). The saturated soil paste extract was prepared and then supernatant samples collected from the saturated pastes were analyzed for electrical conductivity of the saturated pastes (ECe) using an EC meter and the concentrations of Na, Ca, and Mg using AAA for the calculation of the sodium adsorption ratio (SAR), according to Richards (1954). Oriented specimens of clay fractions were prepared and then types of clay mineralogy were identified using an X-ray diffraction technique (Whittig and Allardice, 1986)

The soil physicochemical property results are shown in Table 2. There were wide ranges in these properties, from extremely acid to strongly alkaline, from low to medium CEC (2.9–13.4 cmol$_c$/kg , very low to medium SOM (1.8–16.1 g/kg) and very low to low exchangeable potassium (11.8–43.0 mg/kg);

Table 2 Some selected properties of studied soil collected from ploughed layer (0–20 cm)

Soil	pH$_w$	CEC (cmol$_c$/kg)	Exchangeable				SOM^3 (g/kg)	Particle size distribution			Soil texture^4
			K (mg/kg)	Ca	Mg	Na		Sand (g/kg)	Silt	Clay	
Pm1	7.1 (0.00)	13.4 (1.34)	43 (2.78)	1185 (12.3)	75 (1.75)	491 (62.7)	10.3 (0.12)	351 (1.66)	244 (1.97)	405 (2.21)	C
Pm2	5.4 (0.00)	10.8 (1.25)	31 (1.06)	1357 (6.0)	150 (2.09)	1976 (49.6)	16.1 (0.22)	423 (2.38)	274 (0.50)	303 (2.88)	CL
Ki1	8.8 (0.01)	6.8 (0.07)	17 (0.82)	1131 (35.9)	27 (0.69)	1126 (54.0)	3.5 (0.10)	749 (2.13)	118 (2.44)	133 (2.74)	SL
Ki2	4.7 (0.01)	3.2 (0.26)	21 (2.77)	164 (2.8)	19 (0.70)	170 (64.9)	11.1 (0.12)	321 (0.39)	497 (0.49)	182 (0.67)	L
Re1	7.8 (0.00)	7.2 (0.07)	19 (0.67)	951 (6.6)	64 (0.71)	3449 (103)	4.4 (0.51)	584 (1.43)	285 (1.68)	131 (1.91)	SL
Re2	6.6 (0.00)	2.9 (0.25)	12 (0.43)	72 (2.4)	9.0 (0.82)	373 (35.5)	11.0 (0.26)	787 (2.21)	123 (2.03)	90 (0.20)	SL
Ud	8.2 (0.01)	7.8 (0.16)	29 (1.19)	363 (8.6)	70 (0.56)	2677 (12.0)	1.8 (0.08)	710 (1.83)	94 (0.92)	196 (1.38)	SL

pH$_w$ = pH in 1:1 deionized water; CEC=cation exchange capacity; SOM=soil organic matter; C= clay, SCL = sandy clay loam, SL = sandy loam, LS = loamy sand, S = sandy.
Values are presented as mean (± SD) from three replicates and soil series abbreviations are detailed in Table 1.

however, the soils were mostly of loamy sand texture with the exceptions of Pm1, Pm2 and Ki2 that were clay, clay loam and loam in texture, respectively. In addition, the studied soils were dominated by kaolinite, apart from substantial amounts of some 2:1 clay minerals found in the Pm and Ki soils (Table 1). The values for ECe, SAR and ESP, as shown in Table 1, indicated that the soils were all saline-sodic, except for Pm1 which was a sodic soil; nonetheless, their salinity and sodicity levels varied greatly in the ranges 1.50–25.2 dS/m for the ECe, 16.9–148.9% for the ESP and 7.6–51.3 for the SAR.

Soil total nitrogen determination and ammonium fractionation

Soil samples were analyzed for total N using the Kjeldahl method with steam distillation and titration (Bremner, 1996). Soil NH_4^+-N sequential fractionation methods were used to fractionate the NH_4^+-N into different forms. A sample (2 g) of each soil was extracted first with 20 mL of deionized water for 30 min, followed by extraction with 20 mL of 1 M potassium chloride (KCl) for 60 min (Keeney, 1982) at a controlled temperature of 27°C. Each extract was centrifuged at 3,500 revolutions per minute (rpm) for 5 min, decanted and quantified for NH_4^+-N colorimetrically based on the indophenol blue method (Baethgen and Alley, 1989), to measure water-soluble and exchangeable NH_4^+-N, respectively; then, the residue was used in the next step. The available NH_4^+-N was estimated from the summation of water-soluble NH_4^+-N and exchangeable NH_4^+-N. The soil residue was removed, finely ground and air-dried, after which 1 g samples were determined for non-exchangeable NH_4^+-N (fixed NH_4^+-N) based on direct measurement (Silva and Bremner, 1966). Each sample was treated with an alkaline potassium hypobromite (KOBr) solution to remove organic compounds and then washed three times with 40 mL of 0.5 M KCl and shaken with 20 mL of hydrogen fluoride (HF)-hydrochloric acid (HCl)-solution for 20 hr to destroy any clay mineral. Next, the NH_4^+-N concentration in the acid extract was determined using steam distillation and titration with 0.005 M HCl. All the measured soil N parameters were calculated on an oven-dry weight basis and were analyzed in triplicate for each soil.

Kinetic release experiments

Since NH_4^+ may be fixed immediately after fertilization, spiked soil samples with NH_4^+-N were specifically prepared for the kinetic release of recently fixed NH_4^+-N. Each spiked soil sample was prepared by treating a normal soil sample with NH_4^+ at the rate of 1,000 mg/kg soil as NH_4Cl and incubated at field capacity for 1 wk at 27°C, before being air-dried. In addition, original air-dried soil samples were characterized for the release of the native NH_4^+-N in the studied soils. The release of NH_4^+-N by both the native and spiked soil samples was performed using the method described by Ranjbar and Jalali (2014), based on triplicates for each soil. In brief, 1 g of each soil was placed in a 50 mL polypropylene centrifuge tube and then suspended in 10 mL of 0.01 M $CaCl_2$ solution. Each suspension was shaken at 270 rpm for 15 min, centrifuged at 5,000 rpm for 5 min and then filtered. This process was sequentially performed 10 times at a constant temperature of 25±2°C. The concentration of NH_4^+-N released in each extraction was measured using the colorimetric method (Baethgen and Alley, 1989). The release of NH_4^+-N with time was fitted using the kinetics Equations 1–3:

$$\text{Parabolic function: } q = a + b\mathrm{t}^{1/4} \qquad (1)$$

$$\text{Power function: } \ln q = \ln a + b \ln t \qquad (2)$$

$$\text{Elovich: } q = a + b \ln t \qquad (3)$$

where q is the cumulative NH_4^+-N released at time t, a and b are constants corresponding to the intercept and slope, respectively, of the curve and were considered to be an indicator of the NH_4^+-N -releasing capacity and the NH_4^+-N release rate, respectively. The coefficient of determination (R^2) was obtained for the least squares regression of measured versus predicted values and was used as the criterion to determine a good model fit. The SE of the estimate was calculated using Equation 4:

$$\mathrm{SE} = [\Sigma(\mathrm{q}-\mathrm{q}^*)^2/(\mathrm{n}-2)]^2 \qquad (4)$$

where q and q^* represent the measured and predicted NH_4^+-N released, respectively, and n is the number of data points evaluated. In addition, the amount of release and fixation of NH_4^+-N depend on the fixation capacity of the soil, which can be determined by complete saturation of fixing sites in the soil with excessive amounts of NH_4^+-N; hence, the cumulative content of released NH_4^+-N at 150 min was used for NH_4^+-N fixation as the percentage of added NH_4^+-N into the spiked soil sample (Nommik and Vahtras, 1982).

Statistical analysis

All analyses were carried out in triplicate and the results were reported as mean values ± SD. Simple correlation coefficients were computed to evaluate relationships between the response variables of the NH_4^+-N release rate constant and the NH_4^+-N concentration in the different fractions with some attributed soil properties. All statistical analyses were performed using the SPSS statistical program (version 26.0; SPSS Inc.; Chicago, IL, USA).

Results and Discussion

Ammonium fractions in salt-affected soils

The distribution of native NH_4^+-N among the different fractions in the salt-affected soils is shown in Table 3. With the exception of the Ud soil, the contribution of fractionated NH_4^+-N to the total concentration of most soils was mainly from the non-exchangeable fraction (60.5–89.0%) while the remaining fractions represented rather similar proportions, contributing 3.1–30.2% and 3.9–28.0% for the water-soluble and exchangeable fractions, respectively. It has been well documented (Steffens and Sparks, 1997; Cavalli et al., 2015) that the content of native fixed NH_4^+-N in different soils is related to parent material, texture, clay content, clay mineral composition, K status of the soil and K saturation of the interlayer f 2:1 clay mineral, and moisture content. As a result, the amounts of native fixed NH_4^+-N are in the ranges 10–90, 60–270 and 90–460 mg/kg for coarse-, medium- and fine-textured soils, respectively (Nieder et al., 2011). Although non-exchangeable NH_4^+-N is generally transformed to the available forms for crops and, thus, plays an important role in plant nutrition, the studied salt-affected soils had low reserves to supply NH_4^+-N for plants, as shown by their low non-exchangeable NH_4^+-N content (Cavalli et al., 2015; Steffens and Sparks, 1997). Among the soils studied, the Ud soil contained far lower amounts of total N and NH_4^+-N; however, the water-soluble fraction in this soil was greater than the other fractions, probably as a result of local management practices, whereas the non-exchangeable fraction clearly dominated in the other soils. Overall, the determined available concentrations of NH_4^+-N levels (water-soluble + exchangeable) in varied from soil to soil in the current study; regardless, the concentrations were insufficient to boost rice yields to those reported for the tropical region (Fageria and Baligar, 2001; Fageria, 2014).

In fact, differences in the fractionated NH_4^+-N concentrations can be attributed to differences in the SOM and total N in the soil, as the dominant N sources for plants. Based on the current results, the SOM was the most important N reservoir source for the plants in the tested salt-affected soils, with a highly positive correlation coefficient ($r = 0.740$, $p < 0.01$) between SOM and non-exchangeable NH_4^+-N, as shown in Figure 1. An attempt was made to relate salinity and sodicity parameters to NH_4^+-N concentrations in the different fractions of the studied soils. Both the SAR and ESP sodicity parameters were negatively correlated with exchangeable NH_4^+-N ($r=-0.549$, $p < 0.01$ and $r=-0.810$, $p < 0.01$, respectively) and non-exchangeable NH_4^+-N ($r=-0.959$, $p < 0.01$ and $r=-0.605$, $p < 0.01$, respectively) fractions, while the ECe was negatively correlated only with non-exchangeable NH_4^+-N ($r=-0.586$, $p < 0.01$), as shown in Fig. 1. Thus, sodicity had a more adverse impact than salinity on the dominant NH_4^+-N source transformation into the different fractions. This might have resulted from ammonifiers being more tolerant to salinity than sodicity (Irshad et al., 2005; Sahrawat, 2008). Thereafter, sodicity was responsible for suppressing the native N mineralization from organic N into NH_4^+-N, which was confirmed by the results of Laura (1977) which showed that the ammonification process was completely inhibited in salt-affected soils when the sodicity level reached 92% of the ESP.

Table 3 Contents of total N and different forms of NH_4^+-N in studied soils

Soil	Total N (g/kg)	Content of fractionated NH_4^+-N						Total NH_4^+-N (mg/kg)	Available NH_4^+-N (mg/kg)	Cumulative NH_4^+-N at 150 min		NH_4^+-N fixation (% of added NH_4^+-N)
		Ws	Exc	Non-exc	Ws	Exc	Non-exc			(mg/kg)	(% of total N)	
		(mg/kg)			(%of total NH_4^+-N)							
Pm1	0.50 (0.04)	5.51 (0.27)	14.86 (0.09)	32.7 (2.02)	10.4	28.0	61.6	53.0	20.4	30.8 (0.24)	6.2	39.3 (1.71)
Pm2	0.57 (0.02)	4.46 (0.21)	5.59 (0.16)	28.0 (1.50)	11.7	14.7	73.6	38.0	10.0	35.9 (0.56)	6.3	36.7 (1.69)
Ki1	0.16 (0.02)	6.47 (0.08)	6.63 (0.02)	20.1 (1.25)	19.5	20.0	60.5	33.2	13.1	31.8 (0.40)	19.9	13.4 (0.26)
Ki2	0.47 (0.02)	3.90 (0.12)	10.22 (0.15)	28.0 (1.34)	9.3	24.3	66.5	42.1	14.1	69.3 (1.68)	14.7	39.4 (2.78)
Re1	0.19 (0.02)	9.65 (0.01)	1.25 (0.07)	21.0 (2.34)	30.2	3.9	65.8	31.9	10.9	26.4 (0.22)	13.9	20.6 (0.86)
Re2	0.50 (0.02)	1.29 (0.06)	3.33 (0.09)	37.3 (3.34)	3.1	7.9	89.0	42.0	4.6	39.2 (0.45)	7.8	10.9 (1.04)
Ud	0.02 (0.01)	7.51 (0.15)	1.71 (0.52)	2.8 (0.84)	62.5	14.2	23.3	12.0	9.2	14.2 (0.09)	70.9	12.1 (1.30)

Ws = water-soluble fraction, Exc = exchangeable fraction, Non-exc = non-exchangeable fraction.

Values are presented as mean (± SD) from three replicates and soil series abbreviations are detailed in Table 1.

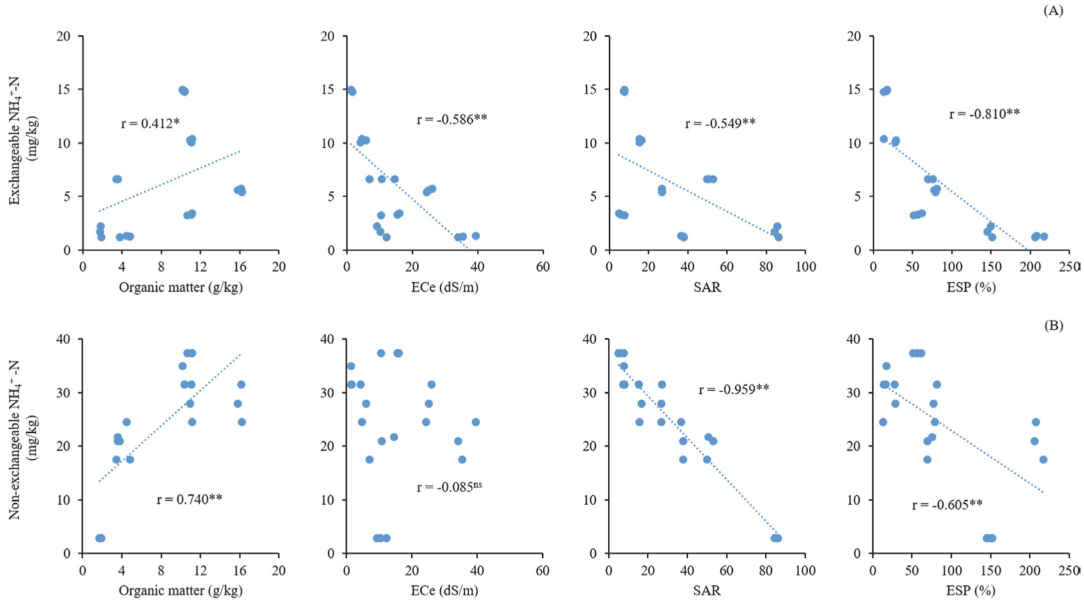

Fig. 1 Linear relationships between selected soil properties with: (A) exchangeable NH_4^+-N; (B) non-exchangeable NH_4^+-N, where $n = 21$, ** = highly significant ($p < 0.01$), * = significant ($p < 0.05$), ns = not significant, r = correlation coefficient of the relationship, ECe = electrical conductivity of saturated paste extract, SAR = sodium adsorption ratio and ESP = exchangeable sodium percentage.

Released ammonium in salt-affected soils

There were differences among the studied salt-affected soils based on the NH_4^+-N released by successive extractions with $CaCl_2$ for 150 min. The cumulative amount of NH_4^+-N released for the entire incubation period was in the range 14.2–69.3 mg/kg, accounting for 6.2–70.9% of the total N content and reflecting low ammonification in these native soils, with exception of the Ud soil (Table 3). This was due mainly to the reduced efficiency of heterotrophic microorganism activity that was retarded by high levels of both salinity (Moussa et al., 2006; Wichern et al., 2006; Bernhard et al., 2007) and sodicity (Laura, 1977; Irshad et al., 2005; Sahrawat, 2008) in the studied soils. This incomplete N mineralization was reaffirmed by the cumulative NH_4^+ being twice as high in the Ki2 soil with the lowest ECe compared to the Pm2, Ki1 and Re2 soils with higher ECe values (Fig. 2), even though these soils similarly contained high total N contents (Table 3). Apart from the salinity and sodicity, the initial soil total N largely determined the amount of NH_4^+released (Lu et al., 2010; Nieder et al., 2011), as indicated by the Ud soil having the lowest cumulative NH_4^+-N content (14.2 mg/kg), as shown in Table 3. The release of NH_4^+-N from all the native soil samples, except Pm2 and Ud, continuously increased until the end of the studied time, whereas the Pm2 and Ud soils reached their plateau levels at 80 and 90 min, respectively (Fig. 2). This suggested that the dominant sinks for NH_4^+-N in most soils from which NH_4^+-N was released are controlled by different rates in the diffusion-controlled process (Feigenbaum et al., 1994; Steffens and Sparks 1997). The release occurred in two phases that could be described by Elovich and heterogeneous models, while additionally, the percentage of non-exchangeable NH_4^+-N released from subsoils was lower than that of topsoils owing to the higher level of native non-exchangeable NH_4^+-N in subsoils which was held more tightly (Steffens and Sparks, 1997). Notably, the NH_4^+-N ions were fixed within 150 min after fertilization, with the amount of NH_4^+-N fixed being in the range 10.9–36.7% of the NH_4^+-N added in the spiked soil samples (Table 3). This reaffirmed that fixation was a rapid process and occurred during the first few hours after fertilization, as reported by Kowalenko (1978), where 50.0–59.0% of the applied NH_4^+-N was fixed during a short time in laboratory and field experiments. Over a wide range of added NH_4^+ (70–2,800 mg/kg), Cavalli et al. (2015) recorded 38–48% fixation in three medium-textured soils. Similarly, Chantigny et al. (2004) stated that NH_4^+-N fixation reached the maximum level during the first day and was greater in clayey soils than in sandy soils.

Table 4 Parameters of models used to describe release kinetics of native and added NH_4^+-N in salt-affected soils

Soil	Native sample				Spiked sample			
	a	*b*	R^2	SE	*a*	*b*	R^2	SE
Power function model								
Pm1	0.66	0.56	0.956	1.48	6.27	0.03	0.818	18.0
Pm2	1.14	0.51	0.979	1.76	6.20	0.05	0.843	13.6
Ki1	-0.57	0.81	0.968	2.81	6.42	0.07	0.839	12.6
Ki2	1.95	0.46	0.916	3.05	6.02	0.08	0.895	27.9
Re1	-0.35	0.73	0.993	1.62	6.17	0.11	0.839	24.1
Re2	1.59	0.41	0.892	2.26	6.51	0.06	0.811	26.6
Ud	-0.06	0.65	0.982	3.16	6.51	0.06	0.846	28.5
Parabolic function model								
Pm1	-1.74	2.76	0.995	0.78	559	4.23	0.711	16.9
Pm2	1.22	3.09	0.860	2.31	546	7.92	0.856	12.0
Ki1	-8.97	3.31	0.895	0.85	699	15.10	0.887	19.8
Ki2	3.59	5.45	0.979	0.64	480	11.79	0.812	20.9
Re1	-5.21	2.55	0.991	0.32	577	19.70	0.892	25.3
Re2	3.76	2.88	0.992	0.59	761	12.18	0.684	30.5
Ud	-2.00	1.95	0.979	5.48	753	11.71	0.729	26.3
Elovich function model								
Pm1	-20.95	10.24	0.979	0.03	524	17.1	0.825	7.7
Pm2	-21.07	11.65	0.977	0.07	483	31.3	0.950	7.1
Ki1	-31.13	12.07	0.947	0.33	585	58.3	0.943	14.1
Ki2	-34.08	20.17	0.977	0.01	387	46.5	0.899	15.3
Re1	-22.71	9.41	0.970	0.06	428	75.8	0.943	18.3
Re2	-15.71	10.57	0.955	0.17	657	49.9	0.818	13.1
Ud	-10.70	5.83	0.992	0.39	655	47.4	0.852	19.4

Constant *a* = NH_4^+-N releasing capacity (mg/kg); constant *b* = NH_4^+-N release rate (mg/kg/min); R^2 = coefficient of determination; SE = standard error of estimate.

Values are means from three replicates and soil series abbreviations are detailed in Table 1.

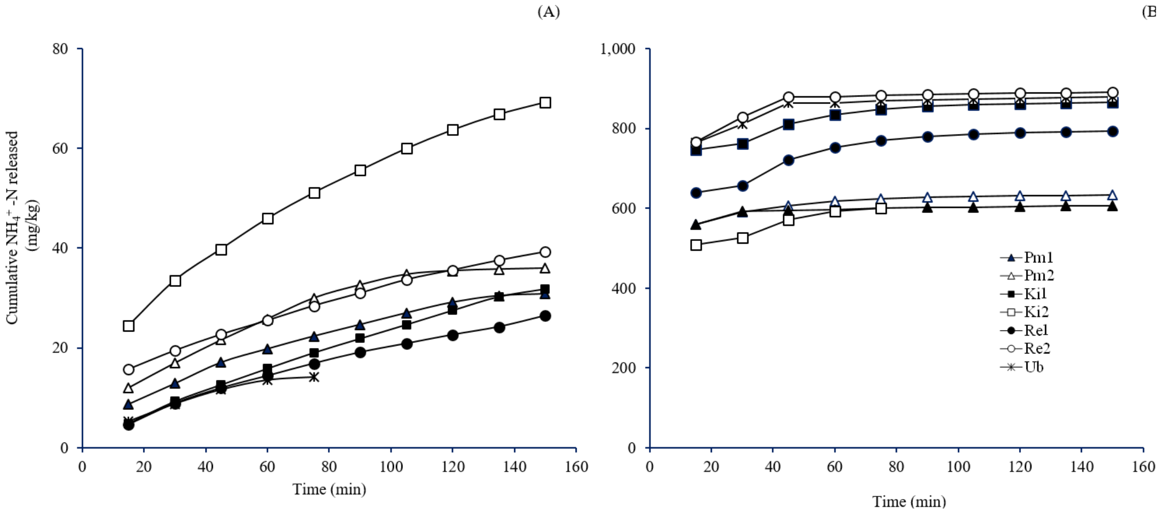

Fig. 2 Cumulative amounts of NH_4^+-N released with time by successive extractions with 0.01M $CaCl_2$ in: (A) native samples; (B) spiked samples, where values are means from three replicates as represented by data points and soil series abbreviations are detailed in Table 1

Regardless of the sample of salt-affected soils, higher NH_4^+-N fixation was detected in soils with a higher clay content, as illustrated by the Pm and Ki2 soils that had the highest clay content (Table 3). This result was expected when coupled with the results from the different clay mineralogical compositions in the studied soils (Table 1). There were substantial amounts of smectite in both the Pm soils and rather moderate amounts of vermiculite in the Ki2 soil, while kaolinite dominated in the other soils. These clay minerals were responsible for this observation. The greater internal surface area in the 2:1 clay minerals (particularly vermiculite) involves abundant sites in the interlayer for fixation of NH_4^+-N (Chen et al., 1989; Steffens and Sparks, 1997), while the hydrogen bonds in the kaolinite minerals prohibit the expansion of interlayer spaces, resulting in the inability to fix NH_4^+-N and producing low fixation of NH_4^+-N (Feigenbaum et al., 1994). However, the fixation rate was reported to be significantly affected by ion diffusion and it decreased with time until the equilibrium was approached (Liang and MacKenzie, 1994). In the current study, this was confirmed by the amount of NH_4^+ in the spiked soil sample being initially released more rapidly within 50 min (more than 60% of the NH_4^+-N added) and then more slowly until the end of the extraction period (Fig. 2). On the other hand, fixed NH_4^+-N fertilization may then be released and converted into soluble and exchangeable forms, thus becoming available for uptake by growing plants when the concentration of available NH_4^+-N decreases based on plant uptake or nitrification (Liu et al., 2008). This also implied that the release of recently fixed NH_4^+-N after was relatively long-term with two phases: a rapid phase attributed to the release of water-soluble and exchangeable NH_4^+-N, followed by a phase where the fixed NH_4^+-N, tightly held by clay minerals which was not readily available for plant uptake, was slowly released, probably being available in the second or third season, as suggested by Lu et al. (2010).

Kinetic release of ammonium and its relationship to soil properties

The kinetic parameters estimated from the various models for NH_4^+-N release in the studied soils are shown in Table 4. None of these models actually predicted the NH_4^+-N releasing capacity of the non-spiked samples due to the negative values of the constant *a*, which is indicative of the potential amount of released NH_4^+-N from the soil N pool to supply N for crops in some soils, particularly in those containing high sand contents. An important term in these equations is the constant *b*, representing the release rate of NH_4^+-N, which was expressed differently in each of the three kinetic models, with each having a high R^2 value. Nonetheless, the Elovich equation provided the lowest SE; therefore, it was selected to describe the kinetic release rate of NH_4^+-N in the studied soils (Fig. 3A) with *b* values in the range 5.82–20.17 mg/kg/min. In addition, based on the R^2 and SE values of the Elovich model, it was used to fit the data of added NH_4^+-N release in the spiked soil samples (Fig. 3B), with the rate of NH_4^+-N release being in the range 17.01–75.85 mg/kg/min. The Elovich equation has been reported to provide a good fit for the release kinetics of NH_4^+-N in different soil types (Steffens and Sparks, 1997; Kithome et al., 1998; Jellali et al., 2010; Ranjbar and Jalali, 2014), as well as describing the kinetic release of other ions, such as K, due to their similar crystalline radius (Jalali, 2006). This model indicated that diffusion was the main process controlling the release of NH_4^+ in the studied soils, with the NH_4^+-N release apparently having a heterogeneous diffusion process coupled with slow diffusion from interlayer positions (Aharoni and Sparks, 1991; Kithome et al., 1998). Notably, there was a much higher potential release amount of NH_4^+-N and a faster release rate of NH_4^+-N in the spiked soil samples compared to the native soil samples in all the studied soils (Table 4). The substantial NH_4^+-N content in the solution phases through fertilization was responsible for this, as indicated by the largest difference in water-soluble NH_4^+-N amongst the NH_4^+-N forms between the native- and spiked soil samples (Fig. 4). Therefore, the mechanism controlling NH_4^+-N release in the spiked soil samples was the large amount of NH_4^+-N initially released rapidly that was attributed to the mass action exchange of water-soluble NH_4^+-N from the external surfaces of clay mineral particles, whereas there was slow release in later stages, indicating that NH_4^+-N was released from internal sites through controlled diffusion. In addition, the low NH_4^+-N release rate by the native soil samples contributed to NH_4^+-N being released from non-exchangeable NH_4^+-N, since it was trapped more in the center of the interlayers (Steffens and Sparks, 1997) resulting in little of it being released compared to that recently fixed from the added fertilizer. Based on the results of the current study, the additional supply of organic material with a high C:N ratio is necessary to encourage an enhanced NH_4^+-N release rate, which in turn ameliorates these salt-affected soils. This was attributed to such organic material enhancing the microbial activity of heterotrophic microorganisms, leading to the rapid consumption of exchangeable NH_4^+-N and even NO_3^--N (Xie et al., 2021), which results in a greater tendency for fixed NH_4^+-N to be released.

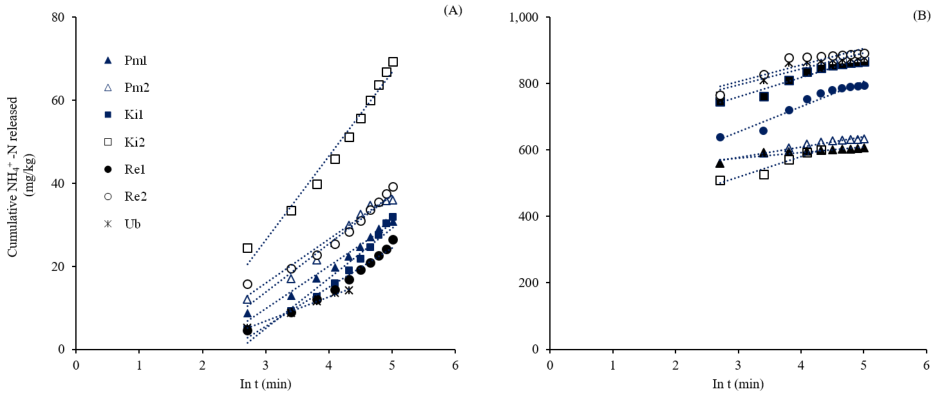

Fig. 3 Relationship between observed and predicted NH_4^+-N released kinetics by successive extractions with 0.01M $CaCl_2$ as described by Elovich model (dotted lines) in: (A) native samples; (B) spiked samples, where values are means from three replicates as represented by data points and soil series abbreviations are detailed in Table 1

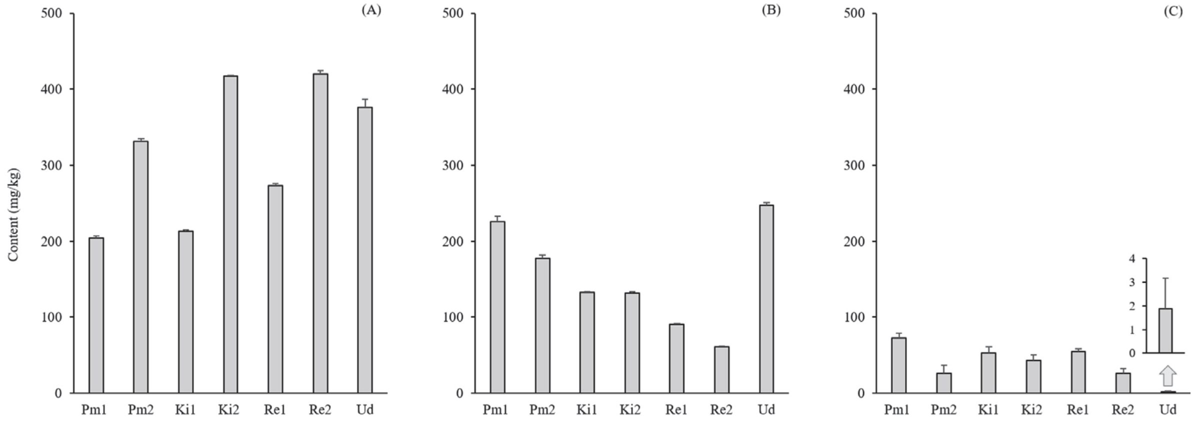

Fig. 4 Different contents of NH_4^+-N in different fractions between spiked and native soil samples: (A) water-soluble NH_4^+-N; (B) exchangeable NH_4^+-N; (C) non-exchangeable NH_4^+-N, where values are means from three replicates as represented by data points, vertical error bars indicate SD and soil series abbreviations are detailed in Table 1.

Table 5 Correlation coefficient (r) between Elovich *b* constant and soil properties

Elovich constant	Soil property parameter				
	Soil pH_w				
b	-0.693**				
	Salinity and sodicity parameters:				
	ECe	SAR	ESP	Exchangeable Na	
b	-0.277	-0.525*	-0.573**	-0.606**	
	Soil N and NH_4^+speciation:				
	Total N	Organic matter	Water-soluble NH_4^+-N	Exchangeable NH_4^+-N	Non-exchangeable NH_4^+-N
b	0.496*	0.461*	-0.418	0.487*	0.454*
	Exchange properties and exchangeable nutrients:				
	Cation exchange capacity		Exchangeable K	Exchangeable Ca	Exchangeable Mg
b	-0.412		-0.206	-0.209	-0.314
	Particle size distribution:				
	Sand	Silt	Clay		
b	-0.552**	0.809**	-0.055		

pH_w = pH in 1:1 deionized water; ECe = electrical conductivity of saturated paste extract; SAR = sodium adsorption ratio; ESP = exchangeable sodium percentage. Asterisks denote significant differences, where * = $p < 0.05$, ** = $p < 0.01$ and $n = 21$.

Increasing the NH_4^+-N concentration in the soil solution causes diffusion of NH_4^+ ions toward the interlayers of clay minerals. The spiked N fertilizer was the major factor which increased the NH_4^+-N concentrations in the soil solutions in this study (Fig. 2). There are other factors affecting the NH_4^+-N concentrations in soil solution, including the physico-chemical properties of the soil, which have been recognized as governing the release of NH_4^+-N (Beauchamp, 1982; Steffens and Sparks, 1997; Lodhi et al., 2009;). This was reaffirmed by the fact that the variability in the release of NH_4^+-N in the current studied soils was essentially governed by many soil properties, as indicated by the significant correlations between the *b* values estimated from the Elovich equation and some soil properties (Table 5). Among the soil properties, a strong r value with a negative relationship ($r>-0.60$, $p < 0.01$) was detected with soil pH and extractable Na. In addition, the SAR, ESP and the sand content had negative correlations with the NH_4^+-N release rate, whereas there were positive correlations for the contents of total N, SOM and silt, as well as exchangeable NH_4^+-N and non- exchangeable NH_4^+-N. Unexpectedly, salinity was not statistically correlated with the *b* value, implying that there was no clear impact of the salinity level on the release rate constant for NH_4^+-N.

The pH level of the soil had the most negative effect on the release of NH_4^+-N due to the increase in negative pH-dependent charges on mineral and organic surfaces, as affected by increasing the pH and the subsequent increase in NH_4^+-N adsorption and fixation (Aharoni and Sparks, 1991). Since there was a low N reservoir to provide N in the studied native soils, their ability to release NH_4^+ was variable. However, the N reservoirs in all the studied soils were low compared to those reported by Ranjbar and Jalali (2014) being in the range of 2.1 to 124.5 mg/kg/min, despite no detectable effect of salinity on the rate of NH_4^+-N release. Apparently, all the sodicity parameters retarded the rates of NH_4^+-N release, with extractable Na having a higher r value than the others and thus being the most influential. This reaffirmed that sodicity played an important role as one of the factors negatively affecting N mineralization in salt-affected soils, which would, in turn, limit the N release under a high sodicity level. To date, the mechanism underlying the low N release rate caused by sodicity is still being developed; however, there could be a protective mechanism for reducing the mineralization of native N that could lower the N release rate (Zhou et al., 2017). The other possible reason was attributed to the factor that affected the stability/persistence of microorganisms in the soil, as in this case increasing soil sodicity suppressed bacteria (Laura, 1977; Irshad et al, 2005; Moussa et al., 2006; Sahrawat, 2008). It was evident that the ability of the soil to supply more N increased with an increasing quantity of total N and NH_4^+-N; hence, the additional supply of labile N is necessary in a soil with low desorbable behavior to encourage an enhanced N release rate, as was the case with the current studied soils.

In conclusion, N plays a crucial role in salt-affected soils which can seriously limit crop production to a larger extent than any other plant nutrient element. The selected soils in this study had inherently low N reserves, despite the NH_4^+-N being mainly in the non-exchangeable fraction. Notably, NH_4^+-N, added to the soil through the application of fertilizers, was fixed rapidly and subsequently released to be readily available for plants after 1 wk of exposure. This process plays a vital role in promoting soil N retention and supply in crop production. Among the three kinetic models investigated, the Elovich model was effective in simulating the release of native and added NH_4^+-N, with controlled diffusion being the major mechanism that regulated the release of NH^+_4. These salt-affected soils behaved differently regarding the NH_4^+-N release rate constants, which were essentially governed by several soil properties, especially soil pH and exchangeable Na that had the most negative influence. In addition, sodicity had a more adverse impact than salinity on the dominant transformation of NH_4^+-N sources into the different fractions; hence, the low rate of NH_4^+-N released in these salt-affected soils was subject to their low quantity of N as the supply source coupled with the sodicity.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

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