

AVAILABLE AMMONIUM AND NITRATE LEVELS OF HIGHLAND SOIL ORDERS IN TURKEY AT DIFFERENT FREEZE-THAW CYCLES

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ABSTRACT

Turkey has diverse climate zones and therefore, number of the freeze-thaw process (FTCS) varies from one region to another. The number is increasing especially in high shear and cold regions and such cycles have significant impacts on available nutrients for plants. The present study was carry out with 5 major soil groups (*Vertisol*, *Chernozem*, *Andosol*, *Leptosol* and *Calcisol*) under field conditions to determine the effects of repeated freeze-thaw processes on available nitrogen (ammonium and nitrate) ($\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$) levels of the soils. Five different nitrogen doses (0, 100, 200, 300 and 400 mg kg^{-1}) were applied to 5 major soil groups in three replications. While the first freeze-thaw process usually increased the ammonium and nitrate nitrogen, the second and further freeze-thaw processes usually reduced available N contents of soils for plants. Current findings revealed that available $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ levels greatly depended on number of freeze-thaw cycles and increasing number of cycles decreased available soil nitrogen levels for plants, thus required higher nitrogen fertilizer levels to supply sufficient nitrogen during the plant-growth periods.

KEYWORDS:

Ammonium, freeze-thaw cycle, nitrate, soil orders

INTRODUCTION

Current global warming and subsequent increasing temperatures inhibit freezing process in soils of some areas and also result in lack of snow cover over the soil surface and consequently increase the number of freeze-thaw cycles and decrease soil resistance against freezing conditions [1]. Freezing occurs at subfreezing temperatures of higher altitudes through various mechanisms within certain soil layers. Decreasing snow cover with ongoing global warming increase the number of

freeze-thaw cycles especially during the frosty periods [2]. Freeze-thaw process accelerates the mineralization of organic nitrogen and consequently increases the ammonium and nitrate concentrations. So inorganic N in the soils increased after cycles of freezing thawing [3]. The freeze-thaw process increased the exchangeable ammonia amounts, but decreased the exchangeable potassium amounts. Freepaz et al. [4] reported that a single freeze-thaw cycle reduced the microbial nitrogen contents but increased organic nitrogen levels. Freeze-thaw process regulates the availability of nitrogen and phosphorus and increasing number of cycles also increases soil mineralization. Researchers also found that the freeze-thaw process increased the ammonium formation in the soil and reported increased total dissolved nitrogen and phosphorus. The present study was carry out to determine the effects of freeze-thaw process on soil available nitrogen amounts (NH_4 and NO_3) based on soil properties.

MATERIALS AND METHODS

Description of the site and material. The present study was carried out with soils of 1880-2030 m altitudes of Turkey. The mean annual temperature, precipitation, evapotranspiration and relative humidity of the region are 6.3°C, 398 mm, 1060 mm and 64%, respectively. The mean (60-years average) air temperatures were 0.8, -5.9, -9.1, -7.8, 2.5, 5.4 and 10.5°C in between November and May, respectively. Soil temperatures at 5 and 10 cm depth were respectively 2.3 and 2.5°C in November, -5.8 and -5.4°C in December, -10.6 and -10.5°C in January, -8.6 and -8.6°C in February, 1.8 and 1.2°C in March, 8.6 and 8.1°C in April, 12.6 and 12.1°C in May. On average, snow remains over the ground for 94 days and the region has 124 rainy days per year. According to FAO, the soils are classified as *Vertisol* (VR), *Chernozem* (CH), *Andosol* (AN), *Leptosol* (LP) and *Calcisol* (CL).

TABLE 1
Some chemical and physical properties of the experimental soils

	<i>Vertisol</i>	<i>Chernozem</i>	<i>Andosol</i>	<i>Leptosol</i>	<i>Calcisol</i>
pH (1:2.5 s/w)	7.22	7.01	7.82	7.30	7.76
CaCO ₃ %	0.37	0.44	1.15	0.98	25.64
Organic matter, %	1.21	1.33	2.43	1.84	2.19
Total nitrogen, %	0.0060	0.0052	0.0122	0.0092	0.0102
CEC, cmol _c kg ⁻¹	25.73	35.64	20.75	22.39	39.56
K, cmol _c kg ⁻¹	2.36	2.12	3.15	2.82	3.25
Ca cmol _c kg ⁻¹	15.24	14.22	14.1	12.14	20.41
Mg cmol _c kg ⁻¹	2.63	2.88	2.5	3.25	2.89
Na cmol _c kg ⁻¹	0.52	0.7	1.22	0.61	1.00
P, mg kg ⁻¹	8.25	10.67	21.25	24.27	12.09
Clay, %	57.82	53.11	28.81	13.86	24.69
Silt, %	23.83	23.59	50.39	32.99	29.30
Sand, %	18.35	23.30	20.80	53.15	46.31
Aggregate stability, %	40.20	48.48	30.25	25.05	50.48
EC, μmhos cm ⁻¹	285	260	470	425	435
Bulk density g cc ⁻³	1.09	1.15	1.22	1.34	1.19

TABLE 2
Availability of NH₄-N in soil groups

Freeze-thaw cycles	Fertilizer kg da ⁻¹	Soil group								
		<i>Vertisol</i>			<i>Chernozem</i>			<i>Andosol</i>		
		NH ₄ mg kg ⁻¹	Ava.* %	Ava.** mg kg ⁻¹	NH ₄ mg kg ⁻¹	Ava.* %	Ava.** mg kg ⁻¹	NH ₄ mg kg ⁻¹	Ava.* %	Ava.** mg kg ⁻¹
	Initial	5.27			6.27			8.53		
	0	8.6 d	15.8	1.4	8.7 e	14.8	1.3	21.7 e	42.7	9.3
	100	37.1 b	27.4	10.2	40.0 d	30.1	12.0	30.6 d	39.8	12.2
3	200	24.3 c	14.2	3.5	60.4 c	39.2	23.7	42.1 c	44.6	18.8
	300	46.1 a	21.9	10.1	76.4 b	45.5	34.7	52.3 b	41.9	21.9
	400	49.6 a	21.5	10.7	98.3 a	45.0	44.2	60.4 a	41.0	24.8
	0	11.4 e	21.1	2.4	24.0 e	40.7	9.8	12.2 d	24.0	2.9
	100	47.1 d	34.7	16.4	46.6 d	35.0	16.3	19.7 c	25.7	5.1
6	200	52.1 c	30.5	15.9	61.2 c	39.6	24.2	20.4 c	21.6	4.4
	300	75.7 b	36.0	27.2	69.9 b	41.6	29.0	38.7 b	31.0	12.0
	400	92.1 a	39.9	36.7	86.6 a	39.7	34.4	46.0 a	31.3	14.4
	0	34.3 d	63.2	21.6	26.2 c	44.4	11.6	17.0 e	33.3	5.7
	100	51.4 c	37.9	19.5	46.6 a	35.0	16.3	26.5 d	34.5	9.1
	200	94.2 a	55.2	52.1	32.8 b	21.2	7.0	31.9 c	33.8	10.8
9	300	88.5 b	42.1	37.3	21.8 d	13.0	2.8	33.9 b	27.2	9.2
	400	89.3 b	38.6	34.5	33.5 b	15.3	5.1	40.7 a	27.7	11.3
		<i>Leptosol</i>			<i>Calcisol</i>					
	Initial	5.20			9.53					
	0	19.0 b	29.2	5.5	16.6 e	28.0	4.7			
	100	12.9 c	16.0	2.1	23.1 d	24.2	5.6			
3	200	17.7 b	16.5	2.9	27.4 c	18.5	5.1			
	300	20.4 a	16.3	3.3	33.2 b	18.0	6.0			
	400	22.4 a	13.3	3.0	40.4 a	19.5	7.9			
	0	33.3 e	51.0	17.0	33.2 d	56.1	18.6			
	100	51.6 d	63.9	33.0	54.1 c	56.8	30.7			
6	200	64.0 b	59.9	38.4	75.2 b	50.8	38.2			
	300	58.4 c	46.7	27.3	90.8 a	49.4	44.9			
	400	84.2 a	49.8	41.9	96.6 a	46.7	45.1			
	0	12.9 e	19.8	2.6	9.4 e	15.9	1.5			
	100	16.3 d	20.2	3.3	18.0 d	18.9	3.4			
9	200	25.1 c	23.5	5.9	45.4 c	30.7	13.9			
	300	46.2 b	37.0	17.1	59.8 b	32.5	19.5			
	400	62.5 a	36.9	23.1	69.9 a	33.8	23.6			

* – % of supplemented fertilizer passed to available form with freeze-thaw cycles,

** – the amount of fertilizer able to be taken by plant

Soil analysis. The soil samples were taken from 0–20 cm depth and some physical and chemical analyses were performed to determine the initial soil properties. Cation exchange capacity (CEC) was determined by using sodium acetate (buffered

at pH 8.2) and ammonium acetate (buffered at pH 7.0) according to Sumner and Miller [5]. The Kjeldahl method [6] was used to determine organic N while plant-available P was determined by using the sodium bicarbonate method of Olsen et al. [7].

Electrical conductivity (EC) was measured in saturation extracts according to Rhoades [8]. Soil pH was determined in 1:2 extracts and calcium carbonate concentrations were determined according to McLean [9]. Soil organic matter was determined using the Smith-Weldon method according to Nelson and Sommers [10]. Ammonium acetate buffered at pH 7 [11] was used to determine exchangeable cations. After extraction, the P, K, Ca, Mg, and Na contents were determined using an inductively coupled plasma spectrophotometer (Perkin-Elmer, Optima 2100 DV, ICP/OES, Shelton, CT 06484-4794, USA). The analysis results for soil physical and chemical properties are provided in Table 1.

Freeze and thaw experiments. Field studies were conducted with *Vertisol* (VR), *Chernozem* (CH), *Andosol* (AN), *Leptosol* (LP) and *Calcisol* (CL) major soil groups in 16 plots in fully randomized block design with 4 N doses (0, 100, 200, 300 and 400 mg kg⁻¹ N) and 4 replications. Each N dose was applied at the beginning of November and incorporated into 0–20 cm soil profile. Plots were 1.5 × 4 m in size and the plant-available soil moisture content was 105.3 mm m⁻¹. Soil moisture contents of the plots were brought to field capacity at the beginning of freeze-thaw cycles. The mean (2 years average) air temperatures were –10.3, –16.2, –18.4, –8.2, –2.0, 3.4 and 6.2°C between November and May, respectively. Soil temperatures at 5 and 10 cm depths respectively were –2.8 and –1.0°C in November, –8.4 and –6.3°C in December, –13.8 and –11.2°C in January, –9.3 and –8.0°C in February, 1.0 and 1.6°C in March, 2.5 and 2.2°C in April, 5.2 and 4.8°C in May and soil moistures at 10 cm depth were 90.15, 102.10, 97.23, 100.30, 122.10, 110.13 and 103.18 mm m⁻¹ between November and May, respectively.

Adsorption-desorption isotherms. Ammonium and nitrogen sorption isotherms of the pre-trial soil samples were determined in triplicates [12]. The corresponding sorption isotherms for each element were quantitatively described by parameters through fitting the experimental data to Langmuir and Freundlich isotherms.

Statistical analysis. The laboratory and field experiments had a randomized complete block design with four replications in the field comprised of soil types (5) and nitrogen doses (5). Analysis of variance (ANOVA) was used to determine the effects of soil type, nitrogen doses and freeze-thaw treatments on NO₃ and NH₄ adsorption-desorption. Duncan's multiple comparison test procedure was used to compare the treatment means and regression analysis was used to assess the effects of treatments.

RESULTS

Effects of freeze-thaw process on soil available ammonium content and adsorption-desorption levels of soils. Considering the effects of the freeze-thaw processes on soil ammonium contents under field conditions, significant variations were observed in soil ammonium contents ($p < 0.01$) with fertilizer levels and freeze-thaw processes. Significant changes were also observed in available ammonium levels of soil groups exposed to 3, 6 and 9 freeze-thaw cycles with different ammonium doses and ammonium availability levels of soil groups increased at 6 freeze-thaw cycles. While the highest soil available ammonium contents were generally observed in 6 cycles, the least levels were observed in 3 cycles (Table 2).

Although varied based on soil groups, supplemented N levels had positive impacts on ammonium amounts passed to soil solution with freeze-thaw cycles until certain implementation levels, but beyond those levels, significant portion of supplemented nitrogenous fertilizers was absorbed based on frequency of freeze-thaw cycles. Considering the amount of NH₄ passed to soil solution through adsorption (Figures 1 and 2), amount of NH₄ in soil solution of *Vertisol* soil order in 126 mg kg⁻¹ NH₄ treatment was 24 mg kg⁻¹; the value was observed as 41 mg kg⁻¹ in 48 mg kg⁻¹ NH₄ treatment of *Chernozem* soil order; as 45 mg kg⁻¹ in 50 mg kg⁻¹ NH₄ treatment of *Andosol* soil order; as 45 mg kg⁻¹ in 53 mg kg⁻¹ NH₄ treatment of *Leptosol* soil order; as 45 mg kg⁻¹ in 51 mg kg⁻¹ NH₄ treatment of *Calcisol* soil order. Beyond these doses, effects of freeze-thaw cycles were more distinctive with increasing NH₄ treatments and increasing number of cycles increased the NH₄ fixation capacities of the soils. Optimum NH₄-N doses were calculated considering the amount of NH₄-N passed to soil solution with NH₄-N treatments and the value was calculated as 218 mg kg⁻¹ for *Vertisol* soil order, 222 mg kg⁻¹ for *Chernozem* soil order; 268 mg kg⁻¹ for *Leptosol* soil order; 230 mg kg⁻¹ NH₄-N for *Calcisol* soil order. Beyond these doses, NH₄-N treatments increased the amount of NH₄-N held by or fixated into soils. Adsorption-desorption tests at different number of freeze-thaw cycles (3, 6 and 9) and different nitrogenous fertilizer doses (0, 100, 200, 300 and 400 mg kg⁻¹) revealed a quadratic relationship for the amount of ammonium in soil solution and amount of ammonium passed to soil solution increased with increasing nitrogen doses. However in this relationship, amount of ammonium passed to soil solution decreased with increasing number of freeze-thaw cycles. Amount of adsorbed and desorbed NH₄-N decreased at the end of 9 cycles (Figures. 1-2).

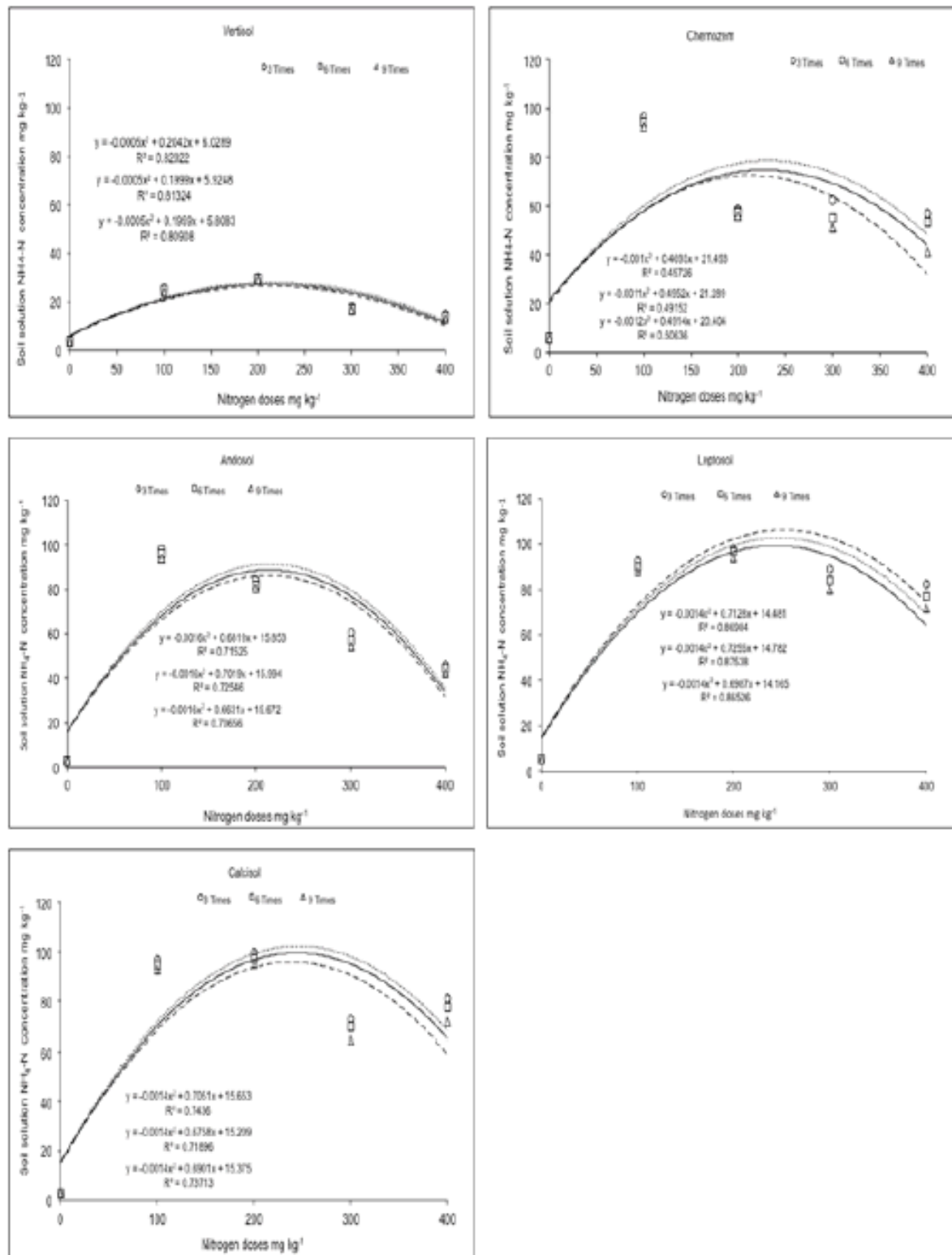


FIGURE 1
NH₄-N levels passed to soil solution through adsorption under field conditions

Effects of freeze-thaw processes on available nitrate contents and adsorption-desorption levels of soils. Considering the effects of freeze-thaw cycles on nitrate contents of soils, significant variations were observed in soil nitrate contents

with fertilizer doses and number of cycles ($p < 0.01$). Significant changes were observed in nitrate availability levels of soils exposed to 3, 6 and 9 cycles with fertilizer doses. Increasing number of freeze-thaw cycles yielded different nitrate availa-

bility levels in different soil orders. While increasing nitrate availability levels were observed in *Vertisol* soil order with number of cycles, generally

decreases were observed in available nitrate levels of *Chernozem*, *Andosol*, *Leptosol* and *Calcisol* soil orders (Table 3).

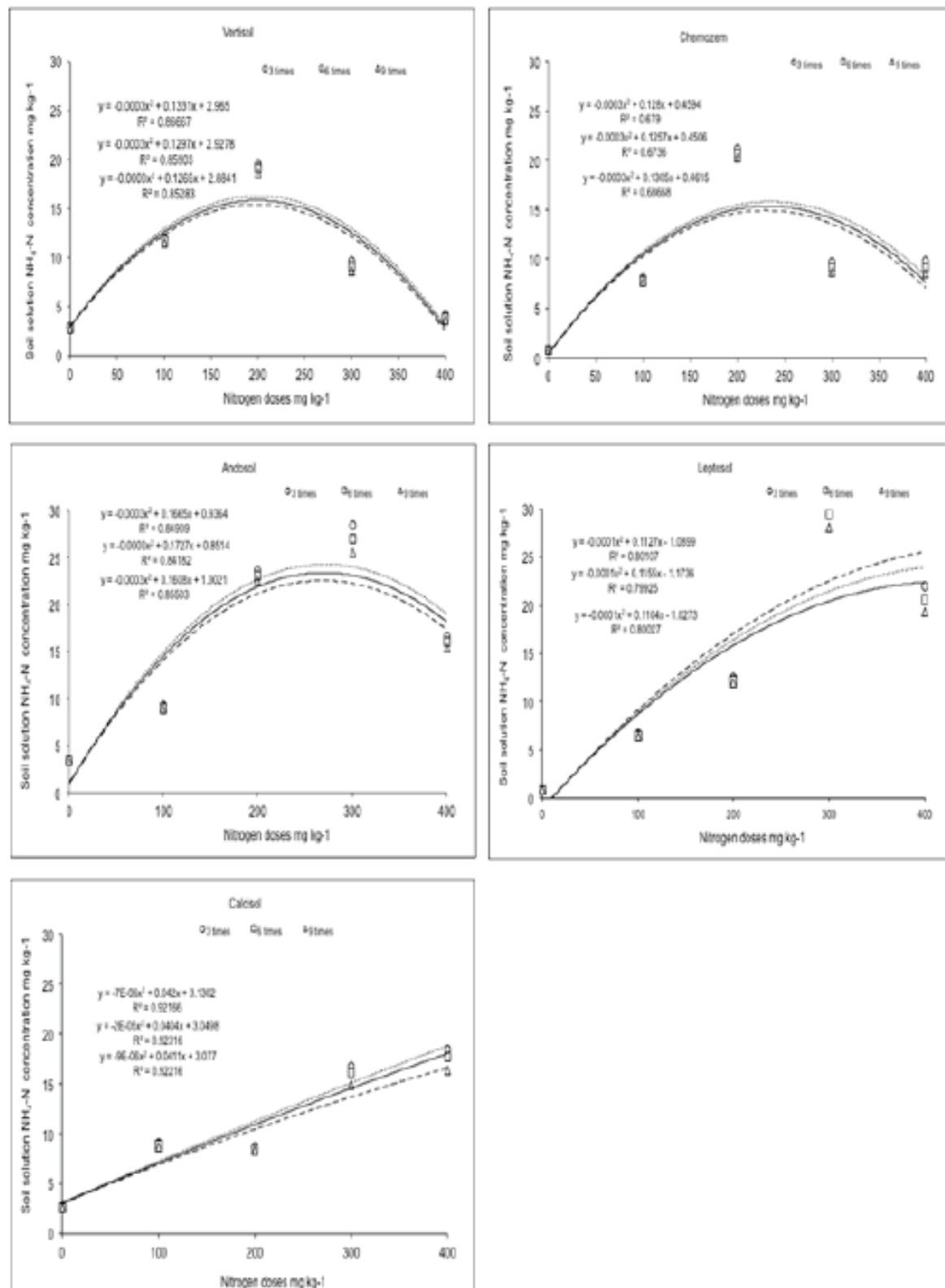


FIGURE 2
NH₄-N levels passed to soil solution through desorption under field conditions

Nitrate adsorption capacities of soil orders exposed to freeze-thaw cycles under field conditions and 0, 20, 40, 60 and 80 kg N da⁻¹ nitrogen doses were assessed at the beginning and end of freeze-thaw cycles and were tried to be expressed for different soil orders (Figures 3-4). N supplementations had positive impacts on amount of NO₃-N passed to soil solution through freeze-thaw cycles until certain levels. However beyond these levels, significant portion of supplemented nitrogenous fertilizers adsorbed based on frequency of freeze-thaw cycles. Amount of NO₃-N passed to soil solution was observed as 24 mg kg⁻¹ in 60 mg kg⁻¹ NO₃-N treatment of *Vertisol* soil order; as 28 mg kg⁻¹ in 68 mg kg⁻¹ NO₃-N treatment of *Chernozem* soil order; as 48 mg kg⁻¹ in 52 mg kg⁻¹ NO₃-N treatment of *Andosol* soil order; as 62 mg kg⁻¹ in 50 mg kg⁻¹ NO₃-N

treatment of *Leptosol* soil order; as 54 mg kg⁻¹ in 52 mg kg⁻¹ NO₃-N treatment of *Calcisol* soil order. Beyond these doses, effects of freeze-thaw cycles were more distinctive with increasing NO₃-N treatments and increasing number of cycles increased the NO₃-N fixation capacities of the soils (Figures 3-4). Optimum NO₃-N doses were calculated considering the amount of NO₃-N passed to soil solution with NO₃-N treatments and the value was calculated as 213 mg kg⁻¹ for *Vertisol* soil order; as 192 mg kg⁻¹ (38 kg N da⁻¹) for *Chernozem* soil order; 215 mg kg⁻¹ for *Andosol* soil order; as 204 mg kg⁻¹ (41 kg N da⁻¹) for *Leptosol* soil order; as 186 mg kg⁻¹ NO₃-N for *Calcisol* soil order. Beyond these doses, NO₃-N treatments increased the amount of NO₃-N held by the soils (Figures 3-4).

TABLE 3
Availability of NO₃-N in soil groups

Freeze-thaw cycles	Fertilizer kg da ⁻¹	Soil group								
		<i>Vertisol</i>			<i>Chernozem</i>			<i>Andosol</i>		
		NH ₄ mg kg ⁻¹	Ava.* %	Ava.** mg kg ⁻¹	NH ₄ mg kg ⁻¹	Ava.* %	Ava.** mg kg ⁻¹	NH ₄ mg kg ⁻¹	Ava.* %	Ava.** mg kg ⁻¹
	Initial	7.17			8.50			10.00		
3	0	15.1 e	29.0	4.4	15.1 e	25.6	3.9	30.9 e	47.1	14.5
	100	28.4 c	39.3	11.1	46.1 d	45.5	21.0	33.5 d	42.3	14.2
	200	21.5 d	22.5	4.9	49.1 c	43.3	21.3	36.1 c	38.1	13.7
	300	36.3 b	32.7	11.8	54.4 b	41.9	22.8	40.6 b	30.0	12.2
	400	46.5 a	29.1	13.5	58.2 a	41.8	24.4	48.9 a	32.8	16.0
6	0	11.3 c	21.7	2.5	20.4 c	34.6	7.1	13.5 e	20.6	2.8
	100	16.6 b	23.0	3.8	27.2 b	26.9	7.3	23.2 d	29.3	6.8
	200	13.6 c	14.2	1.9	28.7 b	25.3	7.3	27.0 c	28.6	7.7
	300	30.2 a	27.2	8.2	28.0 b	21.5	6.0	75.3 a	55.7	42.0
	400	27.2 a	17.0	4.6	36.3 a	26.1	9.5	50.2 b	33.6	16.9
9	0	25.7 d	49.3	12.7	23.4 d	39.7	9.3	21.3 c	32.4	6.9
	100	27.2 d	37.7	10.3	28.0 c	27.6	7.7	22.5 c	28.5	6.4
	200	60.5 b	63.2	38.2	35.5 b	31.3	11.1	31.6 b	33.3	10.5
	300	44.6 c	40.1	17.9	47.6 a	36.6	17.4	19.3 d	14.3	2.8
	400	86.2 a	53.9	46.5	44.6 a	32.1	14.3	50.2 a	33.6	16.9
		<i>Leptosol</i>			<i>Calcisol</i>					
	Initial	6.27			10.47					
3	0	29.3 d	36.4	10.6	18.0 d	25.2	4.5			
	100	41.2 c	42.8	17.6	40.6 c	43.0	17.4			
	200	54.5 b	48.2	26.3	71.8 b	57.4	41.3			
	300	53.2 b	49.4	26.3	75.8 a	50.0	37.9			
	400	56.5 a	45.5	25.7	70.5 b	44.5	31.4			
6	0	33.3 c	41.3	13.7	41.2 a	57.9	23.9			
	100	37.9 b	39.3	14.9	40.6 a	43.0	17.4			
	200	35.9 b	31.8	11.4	29.3 b	23.4	6.8			
	300	35.2 b	32.7	11.5	23.3 c	15.4	3.6			
	400	38.6 a	31.0	12.0	27.9 b	17.6	4.9			
9	0	18.0 d	22.3	4.0	12.0 d	16.8	2.0			
	100	17.3 c	17.9	3.1	13.3 d	14.1	1.9			
	200	22.6 b	20.0	4.5	23.9 c	19.1	4.6			
	300	19.3 c	17.9	3.5	52.5 b	34.6	18.2			
	400	29.3 a	23.5	6.9	59.9 a	37.8	22.6			

* – % of supplemented fertilizer passed to available form with freeze-thaw cycles,

** – the amount of fertilizer able to be taken by plant

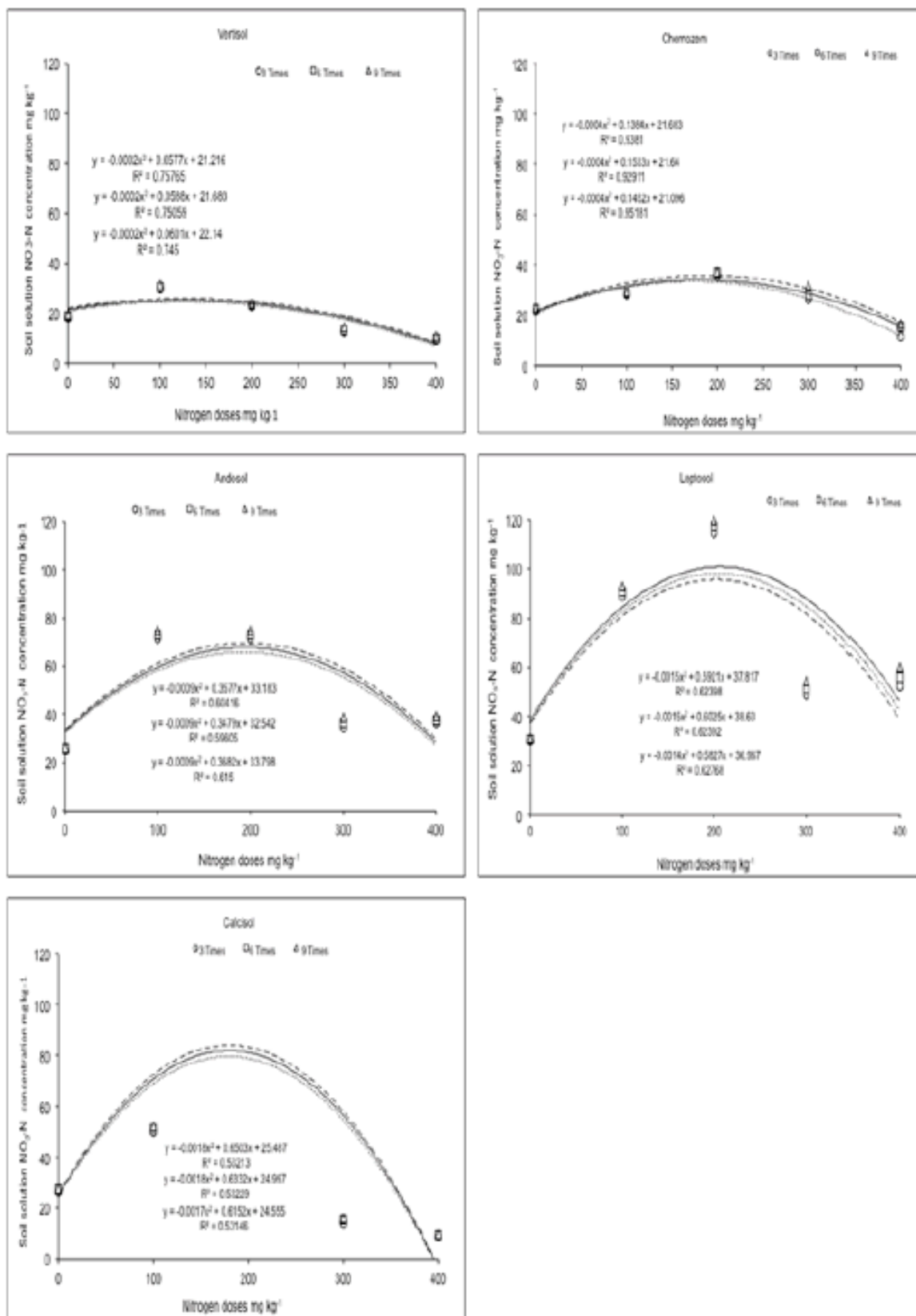


FIGURE 3
NO₃-N levels passed to soil solution through adsorption under field conditions

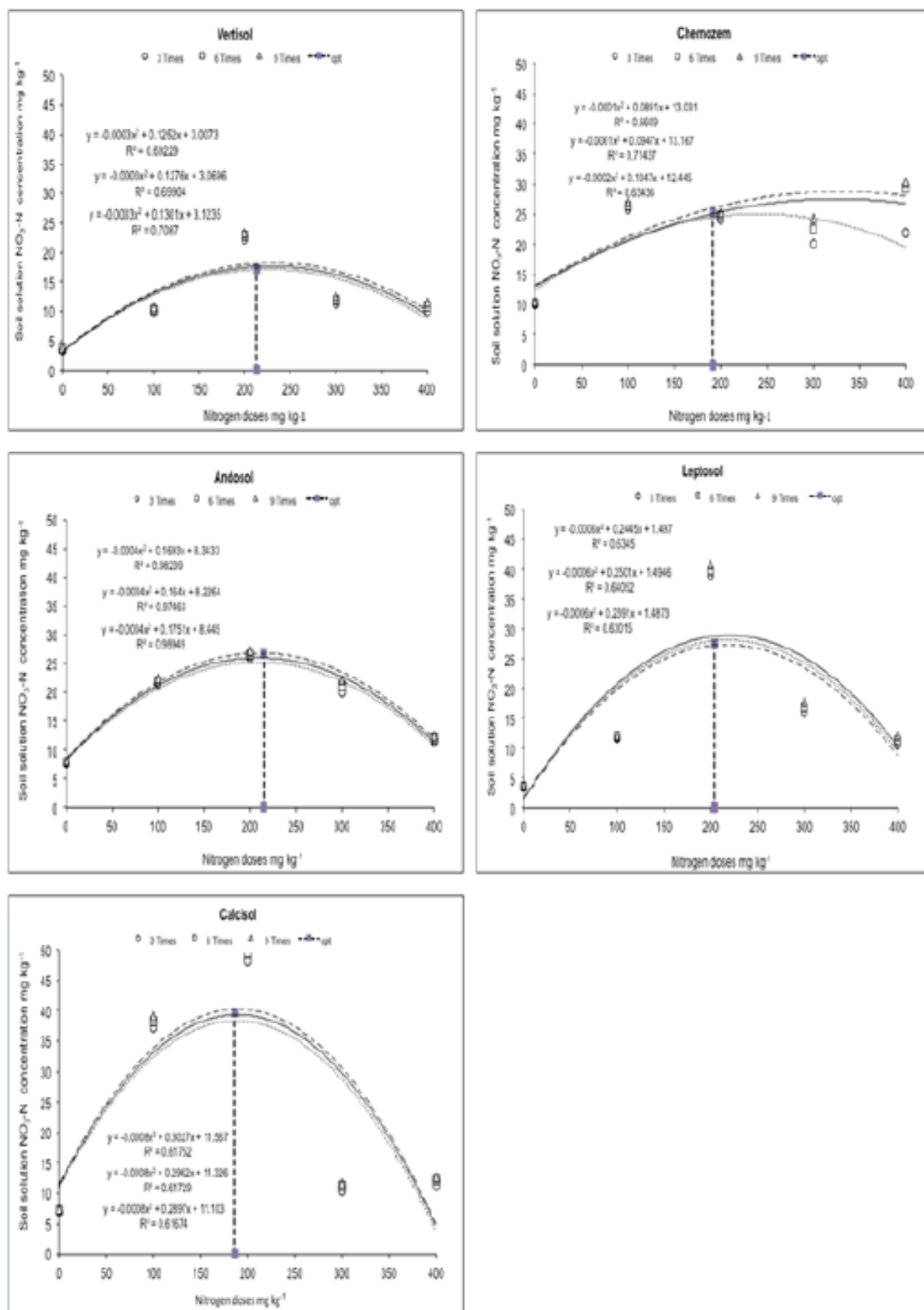


FIGURE 4
NO₃-N levels passed to soil solution through desorption under field conditions

DISCUSSION

The present study was conducted for two years to investigate the effects of freeze-thaw processes on available nitrogen contents of 5 large soil orders. Results revealed significant decreases in $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ contents of soils with increasing number of freeze-thaw cycles. Previous studies also reported similar findings. Urakawa et al. [13] indicated that increasing freeze-thaw frequency effected form transformation of nitrogen and such a case had remarkable impacts on soil fertility when it happened especially during the development period. Freeze-thaw cycles are usually observed in soils with slight snow cover [14]. Frequent freeze-thaw processes leads to the death of bacteria required for the mineralization of soil organic matter or for the conversion of total nitrogen into NH_4 and NO_3 nitrogen [3]. As a result of death or inactivity of soil microorganisms, significant decreases are observed in available portions of plant nutrients in soils. In the present study, significant decreases were observed in available nitrogen contents with increasing number of freeze-thaw cycles (9 times) and such results were similar to the findings of Zhou et al. [3].

Aggregate disintegration speeds up with the increase in frequency of freeze-thaw cycles and resultant compaction in plant root regions results in death of healthy roots [15, 16, 17]. Death of roots and other similar unfavourable conditions decrease the availability of nutrients and mineralization of soil organic material [18] and increase unavailable forms or fixated nutrients in soils [3, 19]. In the present study, amount of fixated NH_4 and $\text{NO}_3\text{-N}$ increased but available portions decreased with increasing number of freeze-thaw cycles. In frozen soils, thawing temperatures activate the microorganisms, which are able to transform into spore forms and not died at freezing temperatures, through the secretions released from the died bacteria and ultimately speed up the conversion of soil nitrogen into inorganic form. However, increasing freeze-thaw frequencies negatively affect the case and decrease the soil microorganism activity to a level much slower than the initial levels [20].

In soil frozen under lower temperatures, reduced microorganism activity may not play a significant role in the amount of available nitrogen not originated from organic material. Amount of applied nitrogenous fertilizers may increase the available nitrogen levels of soils [4]. Since soil aggregate stability is spoiled up with freeze-thaw processes, the $\text{NH}_4\text{-N}$ hold by soil colloids is freed and consequently available N contents increase. In the present study, while an increase was observed in available NH_4 and $\text{NO}_3\text{-N}$ levels based on soil characteristics and applied fertilizer with 6 freeze-thaw cycles, available NH_4 and $\text{NO}_3\text{-N}$ levels decreased with 9 freeze-thaw cycles and such results were

similar to findings of previous studies [15]. The present results revealed that freeze-thaw processes had significant impacts on soil nitrogen adsorption and desorption capacities. Previous studies also reported significant increases in adsorption capacities but decreases in desorption capacities with increasing number of freeze-thaw cycles [21].

Amount of nitrogen passed to soil solution or adsorbed-desorbed amount of nitrogen may decrease or increase based on microbial activity, supplemented fertilizer, organic matter content and root secretions [22]. Beside N sorption, freeze-thaw processes affect all these characteristics.

In the present study carried out under field conditions, significant variations were observed in NH_4 and $\text{NO}_3\text{-N}$ contents of 5 different large soil groups with different soil characteristics with the supplemented nitrogenous fertilizer doses.

Current global warming trends increased the number of freeze-thaw cycles and negative cases like insufficient or less snow covers resulted in significant decreases in available nitrogen levels of the soils.

The present study was carried out for two years and increasing number of freeze-thaw cycles decreased the available nitrogen levels and increased adsorbed and fixated amount of nitrogen. Together with organic matter contents, improvements in some physical and chemical soil characteristics may diminish the negative impacts of freeze-thaw processes on available nitrogen contents of soils.

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