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ROLE OF FREEZE-THAW CYCLES IN AVAILABLE Fe LEVELS OF SOME HIGHLAND SOIL ORDERS

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ABSTRACT

Frequency and efficiency of freeze-thaw cycles (FTTCs - freezing and thawing treated cycles) are increasing over soils of cold regions or high altitudes as a natural outcome of global warming. Such cases result in significant changes in available macro and micro nutrient contents of soils. Very little information is available about the effects freeze-thaw cycles have on the availability of soil micronutrients. Therefore, the present study was conducted to determine the effects of frequency of freeze-thaw cycles on available micro nutrient contents of Pellustert, Argiustoll, Haplustept, Fluvaquent and Calciorthid large soil orders of Northern Turkey. Results revealed significant effects of freeze-thaw cycles on available micro nutrient contents of soils mostly based on soil characteristics. The highest Fe content was observed in step 3 of Pellustert soil order (Step 3; each soil was kept at -10, -15, and -20 °C for a month, at -10 °C for 15 days, -5 °C for 15 days, 0 °C for 15 days, then thawed at +2.5, +5, +7.5 and 10.0 °C for 18 hours. This freeze-thaw cycle was repeated 3, 6, and 9 times). It was concluded that the effects of freeze-thaw cycles on Fe availability varied mainly based on soil characteristics and increased frequency of freeze-thaw cycles increased Fe-fixation to soil.

KEYWORDS:
Freeze-thaw cycle, micro nutrient availability, soil orders, soil temperature

INTRODUCTION

As a natural outcome of global warming, freeze durations in cold regions and high altitudes are prolonged and consequently the frequency of freeze-thaw cycles (FTTCs) increased [1, 2]. Previous researches clearly indicated the impact of such cycles on soil nutrient contents and physical structure, especially texture and aggregate stability [3, 4, 5, 6, 7, 8]

Peltovuori and Soinne [9] reported that freeze-thaw cycles destroyed organomineral complexes and consequently freed organic compounds and newly formed surfaces resulting in absorption of nutrients in soil solution. Researchers indicated the significance of freeze-thaw cycles in nutrient availability especially in soils with high organic matter and clay content. Direct chemical effects of freeze–thaw cycles such as precipitation reactions combined with changes in microbial activity linked to physical changes in soil structure may decrease nutrient availability [10, 11]. Freeze-thaw cycles have significant effects also on soil chemical reactions, nutrient availability and transport [12]). Such cycles generally increase ammonium and nitrate concentrations and speed up mineralization of organic nitrogen [13]. Hinman [14] pointed out that freeze-thaw cycles increased exchangeable ammonium levels but decreased exchangeable potassium levels. Additional substrates can be produced from fragmented aggregates through the physical processes of freezing [15, 16, 17]. Herrman and Witter [17] reported that dissolved substances could easily be transferred to available portions with freeze-thaw cycles and 65% of carbon manifestation was realized with microbial mass.

The present study was conducted to determine the effects of freezing duration, number of freeze-thaw cycles, and freezing temperatures on available Fe contents and to compare the effects of excessive number of cycles on Fe levels based on soil characteristics.

MATERIALS AND METHODS

The research was carried out with Fluvaquent, Argiustoll, Pellustert, Calciorthid and Haplustept large soil orders classified and representing Entisol, Mollisol, Vertisol, Ardisol and Inceptisol soil orders.

Laboratory experiments. Experiments were conducted with the soil samples taken from the 0-20 cm layer of fluvaquent, argiustoll, pellustert, calciorthid and haplustept large soil orders. Before the experiments, soil samples were subjected to some physical, chemical, and microbiological analyses. Then, samples were sieved through an 8 mm sieve, stored in 500 g plastic bags, and made ready for experiments. The samples were subjected to Fe treatments based on initial Fe contents. Fe was applied in 0 (control), 1, 3, 6 and 9 mg kg^{-1} doses in the form of $FeSO_4$. Micro element-treated samples were brought to field capacity moisture level, wrapped in stretch films, and exposed to freeze-thaw cycles. The long-term (60 years) average air temperature has been reported to be -10, -15, and -20 °C for December, January, and February, respectively; the actual average air temperature ranged between 0-10 °C (+2.5, +5, +7.5, and +10°C) and the average number of hours exposed to the sun and hours of thawing per day, respectively, were 18 h and 6 h for March, April, and May. Therefore, the laboratory study was conducted in three steps (Step 1, Step 2, and Step 3).

Field experiments. The field experiments were conducted by using the major soil orders of Pellustert, Argiustoll, Haplustept, Fluvaquent, and Calciorthid. Experiments were conducted in randomized complete block design with four replications at the beginning of November. Iron micro nutrient fertilizer for each soil group was applied and mixed in to 0-20 cm of soil profile with field cultivators. Individual plots were 1.5 x 4 m in size. The available moisture content of the soil was 105.3 mm m^{-1}. All of the plots were rain-fed in field conditions and irrigated in laboratory conditions with tap water (Class C_2S_1) with an electrical conductivity of 0.27 dS m^{-1}, a sodium absorption ratio of 0.42, and a pH of 7.6. Soil moisture content of all plots was increased to the field capacity at the beginning of freeze-thaw cycles.

Soil sampling was performed from the 0-10 cm soil layer every 15 days and soil moisture content and temperature were measured.

Soil analysis. Soil samples were taken from 0–10 cm depths to determine chemical and physical properties. Soil samples were air dried, crushed, and passed through a 2 mm sieve prior to chemical analysis. Cation-exchange capacity (CEC) was determined using Na acetate (buffered at pH 8.2) [18]. Exchangeable cations were determined using NH4 acetate (buffered at pH 7.0) [19]. The Kjeldahl method [20] was used to determine total N content or concentration including organic N while plant-available P was determined by using Na bicarbonate [21]. Electrical conductivity (EC) was measured in saturation extracts [22]. Soil pH was determined in 1:2 extracts and $CaCO_3$ concentrations were determined according to McLean [23]. Soil organic matter (OM) was determined using the Smith-Weldon method [24]. A solution of NH_4 acetate buffered at pH 7 [18] was used to determine exchangeable cations. Following the extractions, P, K, Ca, Mg, and Na concentrations were determined using an inductively-coupled-plasma spectrophotometer ICP (Perkin-Elmer, Optima 2100 DV, ICP/OES, Shelton, CT 06484-4794, USA). The analysis results of soils are given in Table 1.

Statistical Analysis. The laboratory and field experiments had a randomized complete block design with three replications in the laboratory and four replications in the field. Experimental variables included soil types (5), iron micro nutrient doses (5), freezing temperature (3), thawing temperature (4) and number of freeze-thaw cycles (3). Analysis of variance (ANOVA) was used to determine the effects of soil type, iron dose, and freeze-thaw treatments on Fe availability; Duncan's multiple comparison test procedure was used to compare the means [25].

TABLE 1
Some chemical properties of soils

		Pellustert	Argiustoll	Haplustept	Fluvaquent	Calciorthid
pH	(1:2.5)	7.30	7.00	7.79	7.29	7.76
$CaCO_3$	%	0.40	0.49	1.20	1.02	25.66
Organic matter		0.91	1.01	2.36	1.41	2.19
Total Nitrogen	mg kg^{-1}	63.00	62.00	119.00	89.00	110.00
NH_4-N		5.70	6.27	8.53	5.20	9.53
NO_3-N		7.17	8.50	10.00	6.27	10.47
CEC	(me 100 gr^{-1})	56.88	55.51	46.76	33.83	39.56
Ca		15.61	14.45	14.08	12.55	12.42
Na		0.54	0.75	1.31	0.66	1.01
Mg		2.70	2.90	2.57	3.16	2.89
K		1.95	1.85	2.62	2.36	2.71
P	mg kg^{-1}	8.23	10.24	21.16	23.62	12.10
Fe		3.78	3.25	2.78	2.33	3.33
Cu		20.65	24.28	24.90	33.77	35.39
Mn		16.19	17.87	14.56	18.05	13.53
Zn		4.24	4.34	4.30	5.18	4.56
B		0.25	0.21	0.39	0.31	11.54

RESULTS

Effects of freeze–thaw cycles on Fe avaliability of soils under field conditions. While the pH of Pellustert, Argiustoll and Fluvaquent soil orders was neutral, pH of Haplustept and Calciorthid soil orders was slightly alkaline. Lime content of Calciorthid soil order was quite high while other orders with lime had low or normal lime levels. Available nitrogen and phosphorus levels were low and medium respectively; K, Ca and Mg levels were sufficient and even high; Fe and Zn levels were each low; Cu and Mn levels were sufficient; B levels were high in Calciorthid soil order and low in other soil orders.

Depending on applied Fe doses, high variations were observed in Fe availibility of soil orders exposed to freeze-thaw cycles 3, 6 and 9 times. Increasing number of cycles generally increased Fe levels of Pellustert, Argiustoll, Haplustept, Fluvaquent and Calciorthid soil orders (Table 2). Increased number of FTTCs resulted in increased available Fe levels of Argiustoll soil order. However in other soil orders, available Fe levels increased up to 6 FTTCs and decreased at 9 FTTCs. The highest available Fe level of Pellustert, Haplustept, Fluvaquent and Calciorthid soil orders was observed in 6 mg/kg Fe dose and at 6 FTTCs.

Considering the fixation capacities of soil orders with $FeSO_4$ fertilization and freeze-thaw cycles, it was observed that increased number of cycles also increased fixation capacities of soil orders. In general, the highest fixation capacities were observed at 9 freeze-thaw cycles (Table 3).

Effects of freeze–thaw cycles on Fe avaliability of soils under laboratory conditions. As a result of freeze-thaw cycles, significant changes were observed in available Fe levels of five large soil orders based on the soil order, number of freeze-thaw cycles, and applied Fe doses ($p<0.01$).

In the first step, while the available Fe contents of Pellustert soil order following 3 freeze-thaw (F-T) cycles at 2.5°C and 5.0°C thawing temperatures were respectively observed as 4.16 and 3.24 mg kg^{-1}, the values were respectively observed as 4.16-4.75 mg kg^{-1} in Argiustoll soil order, as 2.41-1.88 mg kg^{-1} in Haplustept soil order, as 2.15-2.40 mg kg^{-1} in Flavuqent soil order, and as 2.28-2.64 mg kg^{-1} in Calciorthid soil order (Table 4).

TABLE 2
Effects of Fe treatments and freeze-thaw cycles on Fe concentrations of five soil orders in field conditions (mg Fe kg^{-1}).

		Pellustert		Argiustoll		Haplustept		Fluvaquent		Calciorthid	
F-T cycles	F.D mg kg^{-1}	Fe mg kg^{-1}	*Avail. %*	Fe mg kg^{-1}	*Avail. %*	Fe mg kg^{-1}	*Avail. %*	Fe mg kg^{-1}	*Avail. %*	Fe mg kg^{-1}	*Avail. %*
Initial		***760***		***721***		***1018***		***920***		***1056***	
	0	3.17 a	38.16	1.79 b	38.87	2.64 b	40.86	3.35 a	24.59	4.46 b	43.45
	1	2.25 b	33.52	1.56 c	36.42	2.01 c	19.44	2.12 c	15.89	4.99 a	48.59
3	3	1.26 c	16.69	1.77 b	25.28	3.05 a	25.95	3.25 c	23.71	3.62 c	28.74
	6	0.98 d	19.95	2.27 a	26.39	1.53 e	16.97	3.23 b	21.15	3.34 d	29.10
	9	1.17 c	20.29	1.55 c	30.25	1.71 d	23.39	3.31 a	23.26	2.53 e	31.59
	0	1.07 e	12.82	1.41 b	30.64	1.57 d	24.30	5.58 d	40.98	2.84 c	27.61
	1	2.33 c	34.71	1.18 c	27.52	6.73 a	64.97	6.81 b	51.05	2.74 c	26.65
6	3	2.16 d	28.69	1.80 a	25.74	6.73 a	57.36	5.70 c	41.66	4.88 a	38.73
	6	2.63 a	53.46	1.18 c	13.72	5.56 b	61.51	6.75 b	44.22	4.43 b	38.53
	9	2.50 b	43.24	1.43 b	27.84	3.90 c	53.32	7.80 a	54.77	2.50 d	31.21
	0	4.08 a	49.02	1.40 d	30.49	2.25 a	34.83	4.68 b	34.42	2.97 c	28.94
	1	2.13 b	31.77	1.55 d	36.06	1.61 c	15.58	4.41 c	33.06	2.54 d	24.76
9	3	4.11 a	54.62	3.42 b	48.99	1.96 b	16.69	4.74 b	34.63	4.10 a	32.53
	6	1.31 c	26.58	5.14 a	59.89	1.95 b	21.52	5.29 a	34.63	3.72 b	32.37
	9	2.11 b	36.47	2.15 c	41.91	1.70 c	23.29	3.13 d	21.97	2.98 c	37.21

TABLE 3
Fixation capacity of soils after Fe fertilizer treatments

Fe Doses mg kg^{-1}	Fe fixation capacity, %														
	Pellustert			Argiustoll			Haplustept			Fluvaquent			Calciorthid		
	3	6	9	3	6	9	3	6	9	3	6	9	3	6	9
1	0.1d	7.9d	10.0d	6.7c	8.8c	10.8c	4.6d	6.7d	8.8d	15.2d	10.0d	18.9d	70.1b	70.8b	71.4b
3	11.6c	13.5c	15.5c	1.2d	2.0d	4.1d	7.8c	9.8c	11.8c	62.7b	63.5b	64.3b	81.2a	81.6a	82.0a
6	55.0b	57.3b	59.5b	35.6b	39.0b	42.1b	35.2b	38.6b	41.7b	46.3c	49.1c	51.6c	81.6a	82.4a	83.7a
9	68.2a	70.2a	72.2a	69.8a	71.6a	73.5a	68.4a	69.6a	70.7a	71.8a	73.6a	75.4a	83.1a	83.8a	85.0a

TABLE 4
Effects of Fe treatments and freeze-thaw cycles

Fe application doses mg kg^{-1}	FTTC	Pellustert		Argiustoll		Haplustept		Fluvaquent		Calciorthid	
		Thaw temperature, °C									
		+2.5	+5.0	+2.5	+5.0	+2.5	+5.0	+2.5	+5.0	+2.5	+5.0
0		4.16c	3.24d	4.16d	4.75c	2.41c	1.88d	2.15c	2.40c	2.28c	2.64c
1		3.89d	3.79c	4.71b	4.21d	2.35c	2.29c	2.54a	2.26d	2.70a	2.49d
3	3 times	4.45b	4.02b	4.44c	4.17d	2.72b	2.46b	2.41b	2.27d	2.56b	2.50d
6		3.97d	4.19b	4.53c	5.49b	2.33c	2.45b	2.36b	2.86b	2.51b	3.15b
9		5.43a	4.75a	4.93a	5.85a	3.25a	2.84a	2.62a	3.11a	2.78a	3.42a
0		4.05d	5.13a	4.08c	4.46d	2.35c	2.98a	2.10d	2.30c	2.23c	2.53c
1		6.70a	3.66c	5.05b	4.95b	4.05a	2.21d	2.72c	2.67a	2.89b	2.94ab
3	6 times	4.85b	4.39b	5.18b	5.06b	2.48c	2.68b	2.81b	2.75a	2.98b	3.03a
6		4.70b	4.33b	5.84a	5.30a	2.76b	2.54c	3.04a	2.76a	3.23a	3.04a
9		4.34c	3.74c	5.53ab	4.77c	2.42c	2.24d	2.95ab	2.54b	3.13a	2.79b
0		5.07a	3.29c	3.89c	4.52c	2.94a	1.90d	2.01c	2.33c	2.13c	2.56c
1	9 times	3.62c	3.53bc	4.52b	5.06b	2.19c	2.13c	2.43b	2.72ab	2.58b	2.99b
3		4.15b	3.75bc	4.87a	5.15b	2.53b	2.29b	2.65a	2.80a	2.81a	3.08a
6		4.14b	3.90b	4.97a	5.39a	2.42b	2.28b	2.59a	2.81a	2.75a	3.09a
9		3.56c	4.45a	4.96a	4.96bc	2.13c	2.66a	2.64a	2.64b	2.80a	2.90b

(Step 1; soil samples obtained from large soil orders were subjected to -10, -15, and -20°C temperatures, treatment were subject to refreezing at -10ºC for 15 d, and then thawed at +2.5 and +5ºC for 18 h, this cycle was repeated 3, 6, and 9 cycles) on equilibrium solution Fe concentration of five soil major groups (mg kg^{-1})

TABLE 5
Effects of Fe application and freeze-thaw

Fe application doses mg/kg	FTTC	Pellustert			Argiustoll			Haplustept		
		+2.5	+5.0	+7.5	+2.5	+5.0	+7.5	+2.5	+5.0	+7.5
0		3.38c	3.95d	4.26e	4.31d	4.14c	4.54b	1.96c	2.29d	2.47d
1		4.06a	4.18c	4.43d	4.70c	4.49b	3.91c	2.45a	2.53c	2.68c
3	3 times	4.01a	4.80b	5.87b	4.86b	4.74a	3.81c	2.45a	2.93b	3.58b
6		3.46c	3.68e	4.66c	5.10a	4.31b	5.11a	2.02c	2.15d	2.73c
9		3.69b	5.50a	6.39a	4.63c	4.89a	5.51a	2.21b	3.29a	3.82a
0		4.74b	4.45c	5.89a	4.00e	3.83c	4.19c	2.75b	2.58c	3.41a
1		4.69b	3.73e	4.32d	4.98b	4.96b	4.70ab	2.83b	2.26d	2.61c
3	6 times	4.14c	4.29d	5.03b	5.10a	4.84b	4.81a	2.52c	2.62c	3.07b
6		4.24c	4.85b	4.64c	4.67c	5.45a	4.98a	2.48c	2.84b	2.72c
9		5.75a	5.09a	4.00e	4.22d	5.27a	4.61b	3.44a	3.04a	2.39d
0		5.60a	4.16d	3.78d	3.67d	3.79d	4.97a	3.25a	2.41c	2.19c
1		4.23d	4.37c	4.42c	4.38c	4.27c	4.92a	2.56c	2.64b	2.67b
3	9 times	4.81c	4.90b	4.67b	4.89b	4.64b	4.21b	2.94b	2.99a	2.86a
6		5.00b	3.90e	4.86a	5.14a	4.72b	5.06a	2.93b	2.28d	2.84a
9		3.01e	5.03a	4.66b	4.93b	4.98a	4.86a	1.80d	3.01a	2.79a

Fe application doses mg/kg	FTTC	Fluvaquent			Calciorthid		
		+2.5	5.0	+7.5	+2.5	+5.0	7.5
0		2.22c	2.14c	2.34c	2.08c	2.52d	2.70d
1		2.53ab	2.41b	2.10d	2.60a	2.78c	2.93c
3	3 times	2.64a	2.57a	2.07d	2.60a	3.22b	3.91b
6		2.65a	2.24c	2.66b	2.15c	2.37e	2.98c
9		2.46b	2.60a	2.93a	2.35b	3.62a	4.17a
0		2.06d	1.97c	2.16c	2.92b	2.84c	3.72a
1		2.68a	2.67b	2.53ab	3.01b	2.49d	2.85cd
3	6 times	2.77a	2.63b	2.61a	2.68c	2.88c	3.35b
6		2.43b	2.84a	2.59a	2.63c	3.12b	2.97c
9		2.25c	2.80a	2.46b	3.65a	3.34a	2.61d
0		1.89c	1.95d	2.56a	3.45a	2.65c	2.39c
1		2.35b	2.30c	2.64a	2.72c	2.90b	2.92b
3	9 times	2.66a	2.52b	2.28b	3.12b	3.29a	3.12a
6		2.68a	2.45b	2.64a	3.11b	2.51d	3.10a
9		2.63a	2.65a	2.59a	1.91d	3.31a	3.05a

(Step 2; soil samples obtained from major each soil treated with treated with -10, -15, and -20°C treatment were subject to refreezing at 10 °C for 15 d, at-5°C for 15 d, and then thawed at +2.5, 5 and 7.5ºC for 18 h, this cycle was repeated 3, 6, and 9 cycles) on equilibrium solution Fe concentration of five soil major groups (mg kg^{-1})

High variations were observed in available Fe levels with applied Fe doses and generally increased available Fe levels were observed with increasing Fe fertilizer doses. Compared to the control treatment without any Fe fertilizer applications, while Fe fertilizer resulted in higher available Fe levels after 3 and 6 F-T cycles, lower available Fe levels were observed after 9 F-T cycles.

Depending on freeze-thaw cycles and Fe doses, the highest available Fe content was obtained from 1 mg kg^{-1} Fe, 6 F-T cycles and 2.5°C thawing temperature (6.70 mg kg^{-1}) in Pellustert soil order; from 9 mg kg^{-1} Fe, 3 F-T cycles and 5.0°C thawing temperature (5.85 mg kg^{-1}) in Argiustoll soil order; from 1 mg kg^{-1} P, 6 F-T cycles and 2.5°C thawing temperature (4.05 mg kg^{-1}) in Haplustept soil order; from 9 mg kg^{-1} Fe, 3 F-T cycles and 5.0°C thawing temperature (3.11 mg kg^{-1}) in Fluvaquent soil order; and finally from 6 mg kg^{-1} P, 6 F-T cycles and 2.5°C thawing temperature (3.23 mg kg^{-1}) in Calciorthid soil order.

In the second step, while the available Fe level of control treatment of Pellustert soil order without Fe fertilization after 3 freeze-thaw cycles was 3.38 mg kg^{-1} 2.5°C thawing temperature, the value increased to 3.95 mg kg^{-1} at 5.0°C and to 4.26 mg/kg at 7.5°C thawing temperatures. Available Fe levels at three different thawing temperatures were respectively observed as 4.31, 4.14, and 4.54 mg kg^{-1} in Argiustoll soil order; as 1.96, 2.29, and 2.47 mg kg^{-1} in Haplustept soil order; as 2.22, 2.14, and 2.34 mg kg^{-1} in Fluvaquent soil order; as 2.08, 2.52, and 2.70 mg kg^{-1} in Calciorthid soil order. In general, increased available Fe levels were observed with increasing thawing temperatures (Table 5).

High variations were observed in available Fe levels with applied Fe fertilizer doses and generally increased available Fe levels were observed with increasing Fe fertilizer doses. Compared to the control treatment without any Fe fertilizer applications, Fe fertilizer resulted in higher available Fe levels after 3, 6, and 9 freeze-thaw cycles. However, the highest Fe levels were observed after 3 F-T cycles and decreases were observed in Fe contents with increasing F-T cycles (Table 5).

TABLE 6
Effects of Fe application and freeze-thaw

Fe application doses mg/kg	FTTC	Pellustert				Argiustoll				Haplustept			
		+2.5	+5.0	+7.5	+10.0	+2.5	+5.0	+7.5	+10.0	+2.5	+5.0	+7.5	+10.0
0	3 times	4.07bc	4.94a	3.74c	4.06b	3.94c	4.40c	4.47a	3.76c	2.36c	2.86a	2.17d	2.35b
1		3.83c	3.46c	3.23c	3.67c	4.26b	4.87b	4.13b	4.89ab	2.32c	2.09c	1.95c	2.22b
3		4.32b	4.14b	4.81b	4.12b	4.35b	5.09a	4.49a	4.99a	2.64b	2.53b	2.94b	2.52b
6		3.90c	4.13b	5.31a	4.14b	4.50b	4.18d	4.48a	5.08a	2.28c	2.42b	3.11a	2.42b
9		5.36a	3.63c	5.37a	5.34a	5.49a	4.45c	3.96b	4.61b	3.20a	2.17c	3.21a	3.19a
0	6 times	3.93c	3.11d	3.31d	3.93d	4.69d	3.93a	4.57b	4.60c	2.28c	1.80c	1.91c	2.28c
1		6.49a	3.62c	4.11c	5.01c	5.06c	3.71a	4.41b	5.22b	3.92a	2.19b	2.48b	3.03b
3		3.97c	3.81bc	5.67b	5.00c	5.36b	3.89a	4.71b	5.65ab	2.43c	2.33b	3.46a	3.06b
6		4.55b	3.99b	6.07a	6.44a	5.55a	3.76a	5.24a	5.94a	2.66b	2.34b	3.56a	3.77a
9		3.91c	4.53a	6.24a	5.97b	5.11c	3.67a	4.56b	5.97a	2.34c	2.71a	3.73a	3.57a
0	9 times	3.80e	4.26c	5.27c	5.16ab	3.16d	4.49a	4.32c	5.46c	2.20b	2.47c	3.05a	2.99b
1		3.96d	5.30b	6.53a	5.27a	3.46c	4.70a	5.26a	5.76b	2.40b	3.20b	3.95a	3.18a
3		5.25b	5.26b	5.25c	5.13ab	3.39c	4.21a	5.36a	5.63b	3.21a	3.21b	3.20a	3.13a
6		4.18c	6.49a	5.55c	4.95b	3.99b	4.73a	4.86b	6.01a	2.44b	3.80a	3.25a	2.90b
9		5.78a	6.50a	6.13b	4.29c	4.69a	4.82a	5.27a	5.62b	3.46a	3.89a	3.67a	2.57c

Fe application doses mg/kg	FTTC	Fluvaquent				Calciorthid			
		+2.5	+5.0	+7.5	+10.0	+2.5	+5.0	+7.5	+10.0
0	3 times	2.03c	2.27bc	2.30b	1.94c	2.16c	2.50c	2.51ab	2.16c
1		2.29b	2.62a	2.22c	2.63a	2.43b	2.88ab	2.42b	2.92a
3		2.37b	2.76a	2.44a	2.71a	2.52b	3.04a	2.66a	3.01a
6		2.34b	2.18c	2.33b	2.65a	2.49b	2.40c	2.54ab	2.94a
9		2.92a	2.37b	2.11d	2.45b	3.10a	2.61b	2.30c	2.72b
0	6 times	2.42c	2.03b	2.35c	2.37d	2.57c	2.23b	2.57c	2.63d
1		2.72b	2.00b	2.37c	2.81c	2.89b	2.20b	2.59c	3.12c
3		2.91a	2.11a	2.56b	3.07b	3.09a	2.32a	2.80b	3.41b
6		2.89a	1.96b	2.73a	3.09b	3.07a	2.16b	2.98a	3.43b
9		2.72b	1.95b	2.43b	3.17a	2.89b	2.15b	2.65c	3.52a
0	9 times	1.63d	2.31c	2.22d	2.81b	1.73d	2.54b	2.42c	3.12a
1		1.86c	2.53a	2.83b	3.10a	1.98c	2.78a	3.09a	3.44a
3		1.84c	2.29c	2.91a	3.06ab	1.95c	2.52b	3.18a	3.40a
6		2.08b	2.46b	2.53c	3.13a	2.21b	2.71a	2.76b	3.48a
9		2.50a	2.57a	2.80b	2.99ab	2.66a	2.83a	3.06a	3.32a

(Step 3; soil samples obtained from major each soil treated with treated with -10, -15, and -20°C treatment were subject to refreezing at -10°C for 15 d, at-5°C for 15 d and at 0°C for 15 d then thawed at +2.5, +5, +7.5 and 10.0°C for 18 h, this cycle was repeated 3, 6, and 9 cycles) on equilibrium solution Fe concentration of five soil major groups (mg kg^{-1})

Depending on freeze-thaw cycles and Fe doses, the highest available Fe content was obtained from 9 mg kg^{-1} Fe, 3 F-T cycles and 7.5°C thawing temperature (6.39 mg kg^{-1}) in Pellustert soil order; from 9 mg kg^{-1} P, 3 F-T cycles and 7.5°C thawing temperature (5.51 mg kg^{-1}) in Argiustoll soil order; from 9 mg kg^{-1} P, 3 F-T cycles and 7.5°C thawing temperature (3.82 mg kg^{-1}) in Haplustept soil order; from 9 mg kg^{-1} P, 3 F-T cycles and 7.5°C thawing temperature (2.93 mg kg^{-1}) in Fluvaquent soil order; and finally from 9 mg kg^{-1} P, 3 F-T cycles and 7.5°C thawing temperature (4.17 mg kg^{-1}) in Calciorthid soil order (Table 5).

In the third step, available Fe level of the control treatment of Pellustert soil order without any Fe fertilization after 3 freeze-thaw cycles was measured as 4.07 mg kg^{-1} at 2.5°C thawing temperature, as 4.94 mg kg^{-1} at 5°C thawing temperature, 3.74 mg kg^{-1} at 7.5°C thawing temperature and 4.06 mg kg^{-1} at 10°C thawing temperature (Table 6).

Available Fe levels at different thawing temperatures were respectively measured as 3.94, 4.40, 4.47, and 3.76 mg kg^{-1} in Argiustoll soil order; as 2.36, 2.86, 2.17, and 2.35 mg kg^{-1} in Haplustept soil order; as 2.03, 2.27, 2.30, and 1.94 mg kg^{-1} in Fluvaquent soil order; and as 2.16, 2.50, 2.51, and 2.16 mg kg^{-1} in Calciorthid soil order.

Increasing available Fe levels were observed in all soil orders with increasing Fe fertilizer doses. Compared to the control treatment without any Fe fertilizer applications, Fe fertilizers resulted in higher available Fe levels after 3, 6, and 9 freeze-thaw cycles. Decreasing available Fe levels were observed with increasing freeze-thaw cycles (Table 6).

Depending on the freeze-thaw cycles and Fe doses, the highest available Fe content was obtained from 9 mg kg^{-1} Fe, 9 F-T cycles and 7.5°C thawing temperature (6.50 mg kg^{-1}) in Pellustert soil order; from 6 mg kg^{-1} Fe, 9 F-T cycles and 10°C thawing temperature (6.01 mg kg^{-1}) in Argiustoll soil order; from 1 mg kg^{-1} Fe, 9 F-T cycles and 7.5°C thawing temperature (3.95 mg kg^{-1}) in Haplustept soil order; from 1 mg kg^{-1} P, 9 F-T cycles and 10°C thawing temperature (3.10 mg kg^{-1}) in Fluvaquent soil order; and finally from 6 mg kg^{-1} P, 9 F-T cycles and 10°C thawing temperature (3.48 mg kg^{-1}) in Calciorthid soil order.

DISCUSSION

The present findings indicated that Fe availability varied with freeze-thaw cycles and increasing number of cycles resulted in decreasing Fe availability levels and increasing Fe fixation levels.

Since bacteria activity in soils is slower or decreases at low temperatures, available portions of plant nutrients in soils also decrease. Bacteria reactivate at thawing temperatures and consequently increase available Fe levels of the soils under low temperature [26]. Thawing also increases available nitrogen and phosphorus levels of the soils and thus plants can take up or absorb these nutrients quite easily [27]. Availability of soil nutrients increases with increasing microbial activity at higher temperatures while nutrient leaching or loss through runoff decreases. Previous researches indicated faster nutrient absorption by plants after the last thawing temperature [28, 29].

Current results revealed that the effects of freeze-thaw cycles on availability of plant nutrients varied based on soil characteristics and climate conditions. Earlier studies also indicated differences in soil microorganisms based on soil characteristics and thus reported significant impacts of freeze-thaw cycles on availability of soil nutrients [28, 30, 31].

Freeze-thaw cycles may also result in loss of organic matter, organic carbon, and some nutrients [32]. Mineralization conditions speed up with disintegration of organic matter and thus nutrient availability increases rapidly. However, increasing number of freeze-thaw cycles not only terminates this rapid increase in nutrient availability [17, 33] but also decrease the availability of plant nutrients in soils [34]. Supporting the results of previous studies, current findings also indicated that increased number of freeze-thaw cycles decreased the available fractions of plant nutrients in soils and transformed them into inaccessible forms.

Calibration of the processes occurring in soils under laboratory conditions was attempted. Throughout steps 1-3, field conditions were simulated as best as possible. Long-term freeze-thaw temperatures were simulated and similar results observed both under field and laboratory conditions [13, 35]. Increasing number of freeze-thaw cycles decreased available Fe levels of the soils and Fe fixation capacity increased in 9 freeze-thaw cycles. However, since the temperatures are continuously changing under field conditions, the results of step 3 of the laboratory conditions were found to be closer to field conditions.

Based on current results, it was concluded that highland soils were the most susceptible soils against global warming and climatic change. Increasing air temperature has resulted in the rise of soil temperature and increased the frequency of soil freeze-thaw cycles during the winters of cool regions and high altitudes. It was observed in this study that climate change-induced frequent free-thaw cycles decreased the available Fe levels of the soils but increased Fe fixation into the soils. Among 5 large soil orders investigated in this study, the highest fixation capacity was observed in Calciorthid soil order and increasing Fe fertilization dozes and freeze-thaw cycles also supported such increases in fixation capacities.

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