

## Article

# Effects of litter decomposition on soil N in *Picea mongolica* forest at different forest ages

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**Abstract:** The seasonal and vertical spatial variation characteristics of total N,  $\text{NH}_4^+-\text{N}$  and  $\text{NO}_3^--\text{N}$  in *Picea mongolica* forest soil were studied for different stand ages. Results showed that: (1)  $\text{NH}_4^+-\text{N}$  in the soil was positively correlated with sample date, soil  $\text{NO}_3^--\text{N}$ , and forest age ( $p < 0.05$ ), and negatively correlated with soil depth ( $p < 0.01$ ).  $\text{NO}_3^--\text{N}$  in the soil was negatively correlated with sample date and forest age ( $p < 0.05$ ), and significantly negatively correlated with soil depth ( $p < 0.01$ ). (2) the  $\text{NH}_4^+-\text{N}$  content is greater than that of  $\text{NO}_3^--\text{N}$  in each soil layer for the three forest ages. The correlation analysis indicated which factors influenced  $\text{NH}_4^+-\text{N}$  and  $\text{NO}_3^--\text{N}$  in the soil. The content decreased during February and November, and increased in May and August. (3) The total N,  $\text{NH}_4^+-\text{N}$ , and  $\text{NO}_3^--\text{N}$  in the forest soils across the three forest ages increased with the depth of the soil layer (0–50 cm), and showed an overall downward trend. The contents of  $\text{NH}_4^+-\text{N}$  in the soil layer from the young forest (0–10 cm, 10–20 cm and 20–30 cm, 30–40 cm, and 40–50 cm) differed significantly ( $p < 0.05$ ), as did the  $\text{NO}_3^--\text{N}$  results ( $p < 0.05$ ), while results from the middle-aged forest and near-mature forest increased with soil layer depth. There was no significant difference in the  $\text{NH}_4^+-\text{N}$  soil content. (4) The  $\text{NH}_4^+-\text{N}$  in the forest soils showed a trend from mature forest > middle-aged forest > young forest. This trend for soil  $\text{NO}_3^--\text{N}$  content is consistent with that of the  $\text{NH}_4^+-\text{N}$  content in the *Picea mongolica* forest soil.

**Keywords:** Horqin sandy land; *Picea mongolica* forest;  $\text{NH}_4^+-\text{N}$ ;  $\text{NO}_3^--\text{N}$ ; Seasonal dynamics

## 1. Introduction

N is a major macronutrient necessary for plant growth and development, as well as the main limiting factor for forest ecosystem productivity [1,2].  $\text{NH}_4^+-\text{N}$  and  $\text{NO}_3^--\text{N}$  are available N that can be directly absorbed and utilized by plants. Changes in their content in the soil directly affect the migration and transformation of soil N and plant productivity [3]. The N,  $\text{NH}_4^+-\text{N}$ , and  $\text{NO}_3^--\text{N}$  contents in the soil of different forest types and surfaces have been found to differ significantly. Many studies have been undertaken on the chemometric characteristics of soil N in forest ecosystems in China and other countries. These include different forest ages [4,5], land use modes [6,7], succession stages [8] altitudes [9,10], tree species [11,12], and more. In recent years, several studies have been conducted on different tree species, as different species have different habitats with different soil physical and chemical properties, soil nutrient composition and distribution within the ecosystem [13,14]. However, few studies have been conducted in the *Picea mongolica* forest at the North China forest ecotone. Therefore, it is of great significance to study the characteristics of seasonal variation in soil N in this forest.

*Picea mongolica* is a tree species native to the northern agropastoral ecotone. This species mainly grows on sunny slopes in the mountains at an altitude of 1300–1500 m. To date, few studies have been conducted on the quantitative characteristics of soil N in this ecosystem with a focus on forest age, soil depth, and seasonality. In this study, analyses of variations in forest age, soil depth, and seasonal dynamic changes are combined. We compared and analyzed seasonal dynamic changes in soils at different levels of *Picea mongolica* forest and examined the migration and transformation tendency for total and available N to provide a scientific basis for the management of the *Picea mongolica* forests. The results from this study can provide a reference for use in the management and cultivation of artificial forests.

2. Materials and Methods

2.1. Site description

The study area is located in the Baiyin Oboo Nature Reserve (43°30'–43°36'N, 117°03'–117°16'E) in Keshketeng county on the eastern edge of Hunshandak Sandy Land, with an area of approximately 1947 km². The region has a temperate grassland climate, with an average annual temperature of -1.4 °C, an average temperature of -23.4 °C in January, and 17.4 °C in July. The average annual frost-free period is 78 days, with an annual precipitation of 360–440 mm, an average annual evaporation of 1035.6 mm, and an altitude of 1300–1500 m. The soil type is gray forest soil, and the flora belongs to the plant distribution area of Mongolia. In terms of plant species composition, common taxa that are present include *Larix decidua* Mill., *Juniperus sabina* var. *davurica* (Pallas) Farjon, *Spiraea aquilegifolia*, *S. dahurica* (Rupr.) Maxim., and *Pinus tabuliformis* Carr.

2.2. Sample plot setting and sample collection

Three forest areas with young, middle-aged, and near-mature *Picea mongolica* forest were selected in the Baiyinaobao National Nature Reserve. In each forest stand, three 10 x 10 m sampling plots that were in full sun, uniformly distributed, and with good vegetation growth were selected. Five sampling points were chosen in an "s" shape within each sample plot. During March, May, July, September, and January 2017, soil samples were collected from five different soil levels, namely 0–10 cm, 10–20 cm, 20–30 cm, 30–40 cm, and 40–50 cm from the three forest types for indoor treatment and analysis.

**Table 1.** Key vegetation parameters of the sampling plots. The data presented here were collected during March 2017. Values presented are the mean±standard error. Soil sample numbers were similar to 15.

forest type				Soil layer (0–30 cm)		
Age of stand	Elevation gradient	Average	Average height	Soil pH	Soil moisture/	Soil temperature
(a)	m	DBH/ cm	m		%	°C
young forest (0~5a)	1344	1.79±2.15	2.06±0.71	7.01±0.12	35.95±0.45	-15.78±2.49
middle-aged forest (5~30a)	1352	8.03±4.81	8.15±1.86	6.67±0.03	42.45±4.13	-14.59±2.61
near-mature forest (30~40a)	1342	14.26±4.12	13.94±2.15	6.69±0.01	17.28±2.61	-15.33±2.42

**Table 2.** Mean air temperature and precipitation in different months.

Months	Mean air temperature (°C)	Mean precipitation (mm)
February 2017	-14.61	0.30
May 2017	14.50	13.3
August 2017	13.16	0.65
November 2017	-13.79	0

Following air drying of the samples indoors, impurity removal, and grinding through a 100-mesh screen, the soil total N,  $\text{NH}_4^+-\text{N}$ , and  $\text{NO}_3^--\text{N}$  were determined. N was determined using  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2$  digestion indophenol blue colorimetry [15].  $\text{NH}_4^+-\text{N}$  was determined using indophenol blue colorimetry [15].  $\text{NO}_3^--\text{N}$  was determined using phenol disulfonic acid colorimetry in China National Standard (determination of  $\text{NO}_3^--\text{N}$  in the forest soils) (ly / y1233-1999).

2.3. Statistical analysis

Excel 2017 and SPSS 22.0 software were used for statistical analysis of data. One-way analysis of variance (ANOVA) and least significant difference (LSD) were used for analysis of variance and multiple comparisons ( $\alpha = 0.05$ ). The Pearson method was used for correlation analysis. Amos 22.0 software was used to establish a structural equation model. The data in Table 3 is the mean±standard deviation.

3. Results and analysis

3.1. Seasonal variation of soil total N content with soil depth and stand age

**Table 3.** Soil ammonium nitrogen and nitrate nitrogen contents and their vertical distribution in different stand ages and times in young forest (Y-F); middle-aged forest (M-F); and near-mature forest (N-F). Different lowercase letters in the same column denote significant differences between soil layers. Different capital letters in the same row denote significant differences across altitudes at the 0.05 level.

times	Soil layer (cm)	Total N (mg·kg <sup>-1</sup> )			NNH <sub>4</sub> N (mg·kg <sup>-1</sup> )			NNO <sub>3</sub> N (mg·kg <sup>-1</sup> )		
		Y-F	M-F	N-F	Y-F	M-F	N-F	Y-F	M-F	N-F
March 2017.	0-10	37.007±1.43	22.733±0.66	26.88±0.23	0.262±0.16	0.112±0.14	0.084±0.02	21.937±11.75	24.028±10.39	25.198±3.29
	10--20	14.917±0.64	13.817±0.29	30.249±0.47	0.133±0.06	0.073±0.04	0.032±0.03	12.81±3.01	11.871±1.63	15.473±10.85
	20--30	12.9±0.52	10.457±0.83	10.377±0.55	0.064±0.02	0.034±0.02	0.029±0.03	9.409±0.58	8.9±0.56	9.98±1.80
	30--40	12.517±0.81	15.96±0.00	12.963±0.06	0.044±0.01	0.028±0.00	0.026±0.00	8.686±0.54	12.862±1.54	9.89±1.12
	40--50	12.023±0.41	12.55±0.00	11.133±0.64	0.038±0.01	0.045±0.03	0.019±0.01	10.373±1.08	10.25±1.33	10.611±3.04
May2017.	0--10	59.95±1.21	30.317±1.44	25.191±0.76	0.182±0.21	0.09±0.04	0.111±0.09	33.572±14.81	22.587±6.16	36.094±12.77
	10--20	62.417±0.64	33.033±1.11	41.75±1.21	0.059±0.01	0.059±0.03	0.133±0.17	38.116±16.38	34.473±15.62	42.668±24.25
	20--30	22.917±1.01	43.367±1.96	27.423±0.92	0.085±0.08	0.112±0.12	0.02±0.01	21.005±1.64	36.094±9.98	40.236±15.46
	30--40	21.227±1.25	21.751±0.35	23.967±0.62	0.126±0.13	0.021±0.02	0.015±0.01	22.466±2.84	30.601±18.72	31.862±14.58
	40--50	23.25±0.87	26.083±1.67	25.323±0.98	0.068±0.05	0.018±0.01	0.017±0.01	20.054±0.54	21.957±2.85	24.118±1.77
July 2017.	0--10	59.55±0.52	31.417±0.46	25.787±0.27	0.061±0.00	0.124±0.00	0.735±0.00	54.385±0.00	31.251±0.00	22.416±0.00
	10--20	62.45±0.69	33.342±0.58	41.163±0.20	0.057±0.00	0.074±0.00	0.057±0.00	59.95±0.00	33.412±0.00	36.194±0.00
	20--30	23.817±0.55	44.433±0.12	26.99±0.17	0.192±0.00	0.332±0.00	0.033±0.00	21.15±0.00	42.597±0.00	23.497±0.00
	30--40	22.15±0.35	21.573±0.04	24.6±0.48	0.306±0.00	0.033±0.00	0.033±0.00	20.55±0.00	21.192±0.00	22.307±0.00
	40--50	23.903±0.27	27.283±0.40	25.603±0.50	0.153±0.00	0.032±0.00	0.025±0.00	19.988±0.00	20.658±0.00	21.497±0.00
September 2017.09	0--10	23.75±0.35	51.03±0.52	38.513±0.28	0.012±0.02	0.083±0.08	0.061±0.07	25.968±5.34	42.308±16.01	27.9±8.46
	10--20	27.133±0.65	63.61±0.00	47.607±0.30	0.019±0.03	0.024±0.02	0.079±0.06	33.048±9.34	39.156±17.72	37.715±12.24
	20--30	25.06±0.10	50.955±0.00	54.35±0.13	0.03±0.04	0.111±0.08	0.058±0.04	22.916±1.90	36.995±12.81	38.525±18.15
	30--40	41.257±0.15	34.385±0.00	25.35±0.29	0.017±0.03	0.035±0.03	0.067±0.11	31.853±7.71	31.592±8.13	33.123±8.73
	40--50	31.131±0.11	33.139±0.00	25.425±0.05	0.037±0.05	0.065±0.02	0.036±0.06	33.078±3.51	34.203±6.24	24.838±9.97
November 2017	0--10	30.755±0.56	12.908±0.22	21.34±0.42	0.049±0.01	0.025±0.04	0.103±0.07	17.253±10.92	20.696±9.41	26.819±5.85
	10--20	17.083±0.30	22.359±0.37	28.003±0.29	0.042±0.00	0.047±0.02	0.093±0.04	9.616±4.24	15.113±4.80	35.734±9.73
	20--30	14.137±0.15	21.052±0.17	13.943±0.36	0.018±0.01	0.046±0.01	0.104±0.06	11.902±1.79	14.548±5.40	11.241±1.95
	30--40	29.39±0.54	11.073±0.24	9.68±0.32	0.031±0.02	0.053±0.03	0.099±0.02	16.791±10.23	11.511±6.26	13.312±4.25
	40--50	23.84±0.33	11.227±0.28	17.132±0.26	0.026±0.01	0.033±0.01	0.071±0.04	15.591±5.06	12.321±1.65	27.179±25.29

During March and November 2017, the total N content of the soils from *Picea mon-golica* forest stands across the three age groups showed a downward trend with increasing soil depth (Table 3). There were significant differences in the total N content between 0–10 cm, 10–20 cm, 20–30 cm, 30–40 cm, and 40–50 cm soil layers ( $p<0.05$ ). During March 2017, the maximum values of the total N across the three stand ages (37.007±0.43 mg/kg,

22.733±0.06 mg/kg, and 26.88±0.23 mg/kg) were recorded from the 0–20 cm soil layer. The minimum values (12.023±0.41 mg/kg, 10.457±0.83 mg/kg, 10.377± 0.55 mg/kg) were recorded from the 30–50 cm soil layer. The average soil total N contents recorded in near-mature, young, and middle-aged forests were 18.32 mg/kg, 17.87 mg/kg, and 15.96 mg/kg, respectively. During November 2017, the maximum value of the total N for the three forest ages (30.755±0.56 mg/kg, 22.359±0.37 mg/kg, and 28.003±0.29 mg/kg) was recorded from the 0–20 cm soil layer and the minimum value was recorded in the 30–50 cm soil layer. The average soil total N contents recorded in young, near-mature, and middle-aged forests in this period were 23.04 mg/kg, 18.01 mg/kg, and 15.72 mg/kg, respectively.

By recording the year, soil depth, forest type, pH value, soil temperature, soil humidity, soil organic matter, litter N content, litter carbon content, and litter C/N content as independent variables, a linear regression fitting model for all n was constructed. From the linear fitting results in Table 4, Figure 1, and Figure 2, there was a good linear fit for the model with a significant *p* value of 0.001. The results are shown in Table 3. The total N content across the three forest ages from May, July, and September 2017 first increased and then decreased with increasing soil depth. There was a significant difference in the total N content between 0–10 cm, 10–20 cm, 20–30 cm, 30–40 cm, and 40–50 cm (*p* < 0.05), during May 2017. The maximum age total N contents for young and near-mature forests (62.417±0.64 mg/kg and 41.75±1.21 mg/kg, respectively) were recorded from the 10–20 cm soil layer. The maximum age total N content from the middle-aged forest was recorded from the 20–30 cm soil layer (43.367±1.96 mg/kg). The minimum forest age was recorded from the 30–50 cm soil layer. The average soil total N contents in the young, middle-aged, and near-mature forests were 37.95 mg/kg, 30.961 mg/kg, and 28.73 mg/kg, respectively. In July, the maximum value of total N in young and near-mature forests (62.45±0.69 mg/kg and 41.16±0.2 mg/kg, respectively) was recorded from the 10–20 cm soil layer. The maximum total N content from the middle-aged forests was recorded from the 20–30 cm soil layer (44.43±0.12 mg/kg). The minimum age for all three forest age groups was recorded from the 30–50 cm soil layer. The average soil total N contents in the young, middle-aged, and near-mature forests were 38.37 mg/kg, 31.61 mg/kg, and 28.82 mg/kg, respectively. In September, the maximum values of total N from the young and the middle-aged forests (41.25±0.15 mg/kg and 63.61±0.01 mg/kg, respectively) were recorded from the 10–20 cm soil layer. The maximum value of total N from the near-mature forest was recorded from the 20–30 cm soil layer (54.35±0.13 mg/kg). The minimum age across the three forest age groups was recorded in the 30–50 cm soil layer. The average soil total N content recorded in the middle-aged, near-mature, and young forests were 46.62 mg/kg, 38.24 mg/kg, and 29.66 mg/kg. In 2017, the total N content across the three forest age groups first increased and then decreased over time. In May and July, the highest total N content was recorded across all three forest age groups.

**Table 4.** Linear fitting table for soil total nitrogen in *Picea mongolica* forest (F-test). The dependent variable was total N.

Model		Sum of squares	Freedom	Mean square	F	significance
1	regression	632256641	10	63225664	2.319	0.013b
	residual	7062498135	259	27268333		
	total	7694754776	269			

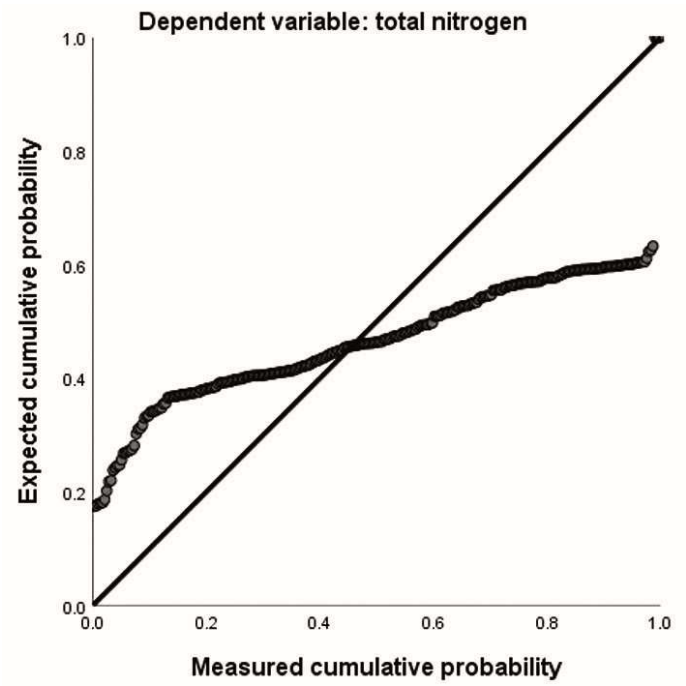


Figure 1. Normal P-P diagram showing regression standardized residuals.

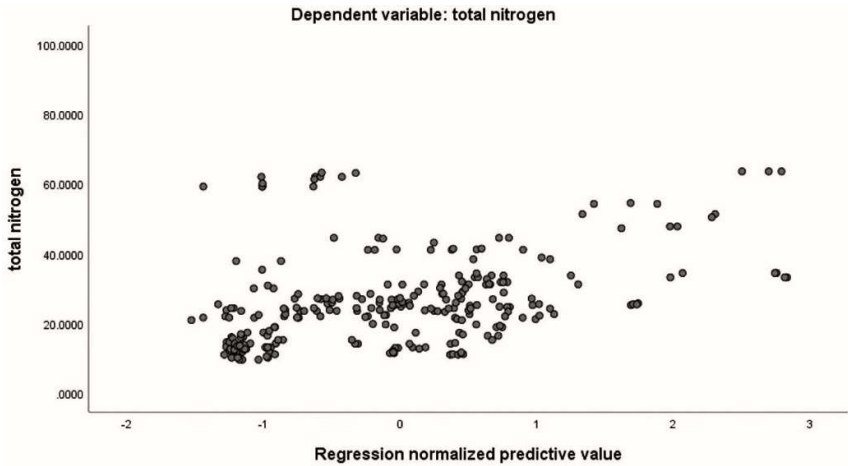


Figure 2. Scatter plot showing total nitrogen.

By recording the year, soil depth, forest type, pH value, soil temperature, soil humidity, soil organic matter, litter N content, litter carbon content, and litter C/N content as independent variables, the linear regression fitting model for all n was constructed. From the linear fitting results in Table 4, Figure 1, and Figure 2, the overall trend of P-P on the linear fitting graph has high linear coverage and normal distribution of the regression value with a significant *p-value* of 0.001. The results are shown in Table 5.

**Table 5.** Multivariate analysis of variance of soil total nitrogen of *Picea mongolica* forest (T-test).

model	Nonstandard Coefficient		Standardization coefficient	t	significance
(constant)	52347.16	27613.11		1.90	0.06
Particular year	-3899.58	1154.61	-1.25	-3.38	0.00
Forest type	-1327.88	550.65	-0.20	-2.41	0.02
Soil depth	5.12	24.72	0.01	0.21	0.08
PH value	-118.22	1006.91	-0.01	-0.12	0.19
humidity	-367.86	390.42	-0.11	-0.94	0.35
temperature	-24.02	78.97	-0.05	-0.30	0.76
Litter N content	-3047.91	3006.83	-0.22	-1.01	0.31
Litter N content	255.93	165.93	1.21	1.54	0.12
Litter CN ratio	-1617.78	569.09	-2.82	-2.84	0.01
Soil organic matter content	8.19	6.66	0.09	1.23	0.22

From the linear fitting results in Table 5, humidity, temperature, and CN ratio of litter and organic matter have had a considerable impact on the level of total N, and the highest contribution rate. Although, the impact of litter N content and pH value is slightly lower, the p-values for all the other influencing factors, except for litter N content, were greater than 0.05, indicating significant results.

3.2. Characteristics of seasonal variation of soil  $\text{NH}_4^+ - \text{N}$  content with soil depth and stand age

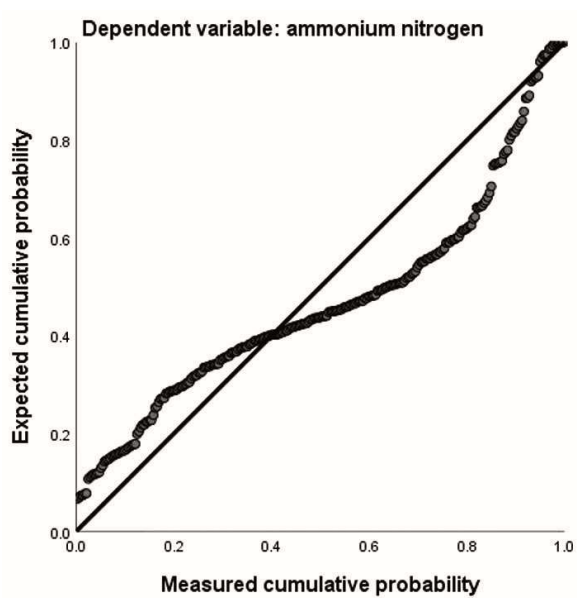
In March and November 2017, the content of  $\text{NH}_4^+ - \text{N}$  in soil for the three forest stand ages showed an overall downward trend with increasing soil depth (Table 3). There were significant differences in the  $\text{NH}_4^+ - \text{N}$  content in the 0–10 cm, 10–20 cm, 20–30 cm, 30–40 cm, and the 40–50 cm soil layers ( $p < 0.05$ ). In March 2017, the maximum values of  $\text{NH}_4^+ - \text{N}$  across the three forest ages ( $0.262 \pm 0.16$  mg/kg,  $0.112 \pm 0.14$  mg/kg, and  $0.084 \pm 0.02$  mg/kg) were recorded from the 0–10 cm soil layer, and the minimum values ( $0.038 \pm 0.01$  mg/kg,  $0.028 \pm 0.01$  mg/kg, and  $0.019 \pm 0.01$  mg/kg) were recorded in the 30–50 cm soil layer. The average soil  $\text{NH}_4^+ - \text{N}$  contents recorded for young middle-aged, and near-mature forests were 0.108 mg/kg, 0.068 mg/kg, and 0.038 mg/kg, respectively. In November 2017, the maximum values of  $\text{NH}_4^+ - \text{N}$  across the three forest ages ( $0.049 \pm 0.01$  mg/kg,  $0.053 \pm 0.03$  mg/kg, and  $0.104 \pm 0.06$  mg/kg, respectively) were recorded from the 0–20 cm soil layer, and the minimum values were recorded from the 30–50 cm soil layer. The average soil  $\text{NH}_4^+ - \text{N}$  content recorded from near-mature, middle-aged, and young forests were 0.094 mg/kg, 0.041 mg/kg, and 0.033 mg/kg, respectively. The  $\text{NH}_4^+ - \text{N}$  content across the three forest ages in May, July, and September 2017 first increased and then decreased with increasing soil depth. The soil total N contents between the 0–10 cm, 10–20 cm, 20–30 cm, 30–40 cm, and 40–50 cm soil layers differed significantly ( $p < 0.05$ ). In May 2017, the maximum value of  $\text{NH}_4^+ - \text{N}$  for young and near-mature forests ( $0.182 \pm 0.21$  mg/kg and  $0.133 \pm 0.17$  mg/kg, respectively) was recorded from the 10–20 cm soil layer. The maximum value of total N ( $0.112 \pm 0.12$  mg/kg) for middle-aged forest was recorded from the 20–30 cm soil layer. The minimum age for the three forest age groups was recorded from the 30–50 cm soil layer. The average soil  $\text{NH}_4^+ - \text{N}$  content recorded from young, middle-aged, and near-mature forests were 0.103 mg/kg, 0.060 mg/kg, and 0.059 mg/kg, respectively. In July, the maximum values of  $\text{NH}_4^+ - \text{N}$  for young and near-mature forests ( $0.306 \pm 0.01$  mg/kg and  $0.332 \pm 0.01$  mg/kg) were recorded from the 10–20 cm soil layer. The maximum value of  $\text{NH}_4^+ - \text{N}$  ( $0.735 \pm 0.01$  mg/kg) from the middle-aged forest was recorded from the 20–30 cm soil layer. The minimum age for the three forest age groups was recorded from the 30–50 cm soil layer. The average soil  $\text{NH}_4^+ - \text{N}$  contents recorded for near-mature, young, and middle-aged forests were 0.176 mg/kg, 0.154 mg/kg, and 0.119 mg/kg, respectively. In September, the maximum values of  $\text{NH}_4^+ - \text{N}$  for young and near-mature forests ( $0.03 \pm 0.04$  mg/kg and  $0.11 \pm 0.08$  mg/kg) were recorded from the 10–20 cm soil layer. The maximum value of  $\text{NH}_4^+ - \text{N}$  ( $0.079 \pm 0.06$  mg/kg) from the middle-aged forest was recorded from the 20–30 cm soil layer. The minimum age for the three forest age



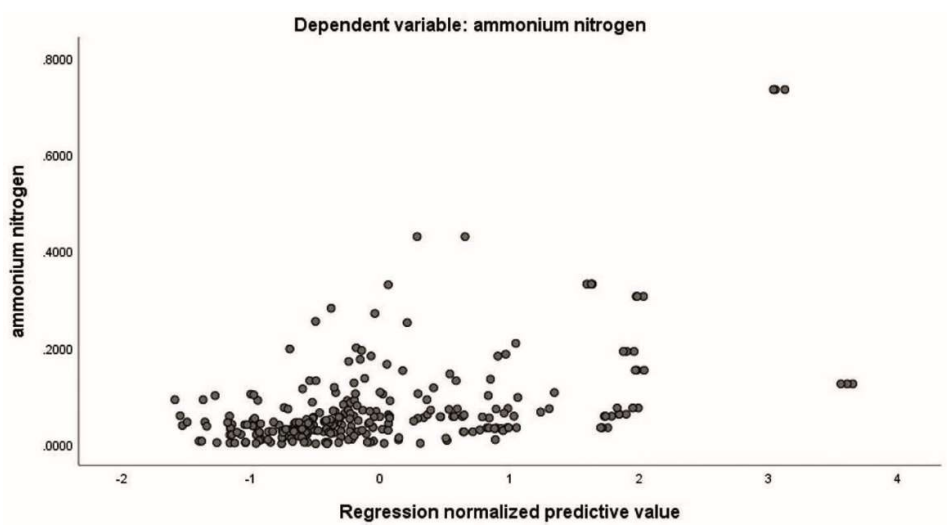
groups was recorded from the 30–50 cm soil layer. The average soil total N contents recorded for middle-aged near-mature, young and forests were 0.063 mg/kg, 0.06 mg/kg, and 0.037 mg/kg, respectively.

**Table 6.** Linear fitting table for soil ammonium nitrogen in *Picea mongolica* forest (F-test).

Model		Sum of squares	Freedom	Mean square	F	significance
1	regression	0.681	10	0.068	8.488	0.001b
	residual	2.079	259	0.008		
	total	2.761	269			



**Figure 3.** Normal P-P diagram of regression standardized residuals.



**Figure 4.** Scatter plot of ammonium-nitrogen prediction.

By recording the year, soil depth, forest type, pH value, soil temperature, soil humidity, soil organic matter, litter N content, litter carbon content, and litter C/N content as independent variables, the linear regression fitting model for all n was constructed. From the linear fitting results in Table 3, Figure 3, and Figure 4, the linear fitting results were

high, the predicted accumulation probability was similar to the actual accumulation probability, the linear coverage rate was high, and there was a normal distribution for the predicted regression value. There was a significant p-value of 0.001. The results are shown in Table 7.

**Table 7.** Multivariate analysis of variance of soil ammonium nitrogen in *Picea mongolica* forest (T-Test).

model	Nonstandard Coefficient		Standardized number		t	Significance
	Beta		Beta			
particular year	0.04	0.02	0.59		2.75	0.05
Forest type	0.02	0.01	0.12		2.54	0.02
Soil depth	0.00	0.00	-0.11		-2.82	0.07
PH value	0.02	0.02	0.09		1.11	0.27
humidity	0.03	0.01	0.53		4.81	0.00
temperature	0.00	0.00	-0.03		-1.23	0.02
Litter N content	0.01	0.05	0.05		0.25	0.80
Litter N content	-0.01	0.00	-1.65		-2.32	0.02
Litter CN ratio	0.03	0.01	2.39		2.66	0.01
Soil organic matter content	0.00	0.00	0.16		2.33	0.02

The linear fitting results in Table 5, including humidity, temperature, and CN ratio of litter and organic matter have a considerable impact on total N, and the highest contribution rate. The impact of litter N content and pH value is slightly lower, but the p-values for all other influencing factors, with the exception of litter N content are greater than 0.05, indicating a significant result.

3.3. Characteristics in seasonal dynamic variation of soil NO<sub>3</sub><sup>-</sup>—N content with soil depth and stand age

During March and November 2017, the soil NO<sub>3</sub><sup>-</sup>—N content across the three forest stand ages first decreased and then increased with increasing soil depth (Table 3). There were significant differences in NO<sub>3</sub><sup>-</sup>—N content between the 0–10 cm, 10–20 cm and 20–30 cm, 30–40 cm, and 40–50 cm soil layers (*p*<0.05). In March 2017, the maximum values for NO<sub>3</sub><sup>-</sup>—N (21.937±11.75 mg/kg, 24.028±10.39 mg/kg, and 25.198±3.29 mg/kg) across the three forest ages were recorded from the 0–10 cm soil layer. The minimum values (8.686±0.54 mg/kg, 8.9±0.56 mg/kg, and 9.89±1.12 mg/kg) were recorded from the 30–40 cm soil layer. The average soil NO<sub>3</sub><sup>-</sup>—N contents recorded in the near-mature, middle-aged, and young forests were 14.23 mg/kg, 13.58 mg/kg, and 12.64 mg/kg, respectively. In November 2017, the maximum values of NO<sub>3</sub><sup>-</sup>—N across all three forest age groups (17.253±10.92 mg/kg, 20.696±9.41 mg/kg, and 35.734±9.73 mg/kg) were recorded from the 0–20 cm soil layer, and the minimum values were recorded from the 30–50 cm soil layer. The average soil NO<sub>3</sub><sup>-</sup>—N contents recorded from the near-mature, middle-aged, and young forests were 22.86 mg/kg, 14.83 mg/kg, and 14.23 mg/kg.

The soil NO<sub>3</sub><sup>-</sup>—N content across the three forest ages during May, July, and September 2017 first increased and then decreased with increasing soil depth. There was a significant difference in the total N content between the 0–10 cm, 10–20 cm, 20–30 cm, 30–40 cm, and 40–50 cm soil layers (*p*<0.05). During May 2017, the maximum values of NO<sub>3</sub><sup>-</sup>—N from young and near-mature forests (38.116±16.38 mg/kg and 42.668±24.25 mg/kg, respectively) were recorded from the 10–20 cm soil layer. The maximum value of NO<sub>3</sub><sup>-</sup>—N from middle-aged forest was recorded from the 20–30 cm soil layer (36.094±9.98 mg/kg). The minimum age across the three forest age groups was recorded from the 30–50 cm soil layer. The average soil NO<sub>3</sub><sup>-</sup>—N contents recorded from near-mature, middle-aged, and young forests were 34.995 mg/kg, 29.14 mg/kg, and 27.04 mg/kg, respectively. In July, the maximum values of NO<sub>3</sub><sup>-</sup>—N from young and near-mature forests (59.95±0.01 mg/kg and 36.194±0.01 mg/kg) were recorded from the 10–20 cm soil layer. The maximum value of NO<sub>3</sub><sup>-</sup>—N from the middle-aged forest was recorded from the 20–30 cm soil layer



(42.597±0.01 mg/kg). The minimum age from the three forest age groups was recorded from 30–50 cm soil layer. The average soil NO<sub>3</sub>–N content recorded for young, middle-aged, and near-mature forests were 35.20 mg/kg, 29.83 mg/kg, and 25.182 mg/kg, respectively. In September, the maximum values for NO<sub>3</sub>–N in young and middle-aged forests (33.048±9.34 mg/kg and 42.308±16.01 mg/kg, respectively) were recorded from the 0–20 cm soil layer. The maximum value for NO<sub>3</sub>–N in near-mature forests (38.523±18.12 mg/kg) was recorded from the 20–30 cm soil layer. The minimum age for the three forest age groups was recorded from the 30–50 cm soil layer. The average soil NO<sub>3</sub>–N content recorded for middle-aged, near-mature, and young forests were 36.85 mg/kg, 29.37 mg/kg, and 24.83 mg/kg, respectively.

In 2017, the soil NO<sub>3</sub>–N increased first and then decreased over time. In May and July, the total N content for the three forest age groups was the highest recorded during the study.

**Table 8.** Linear fitting table for soil nitrate nitrogen in *Picea mongolica* forest (F-test). The dependent variable was nitrate (N).

Model		Sum of squares	Freedom	Mean square	F	significance
1	regression	1348848.91	10	134884.89	2.98	0.001b
	residual	11727318.02	259	45279.22		
	total	13076166.93	269			

By recording the year, soil depth, forest type, pH value, soil temperature, soil humidity, soil organic matter, litter N content, litter carbon content, and litter C/N content as independent variables, the linear regression fitting model for all n was constructed. From the linear fitting results in Table 4, Figure 5, and Figure 6, the linear fitting result did not have a strong fit. Although the linear trend change is presented, the line coverage rate is relatively low. The forecast regression value normal distribution is clear, but still has the specific reference value. The *p*-value is significant at 0.001. The results are shown in Table 9.

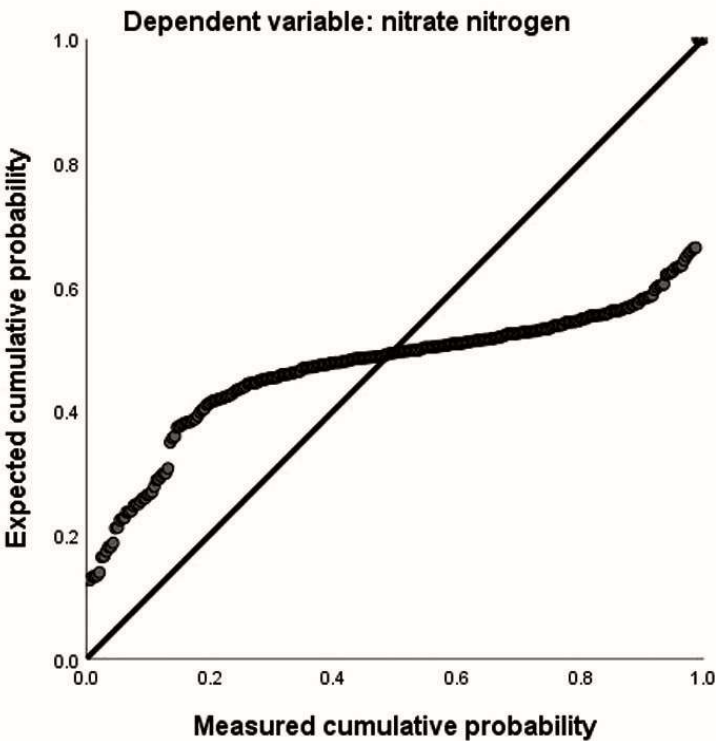


Figure 5. Normal P-P diagram of regression standardized residuals. .

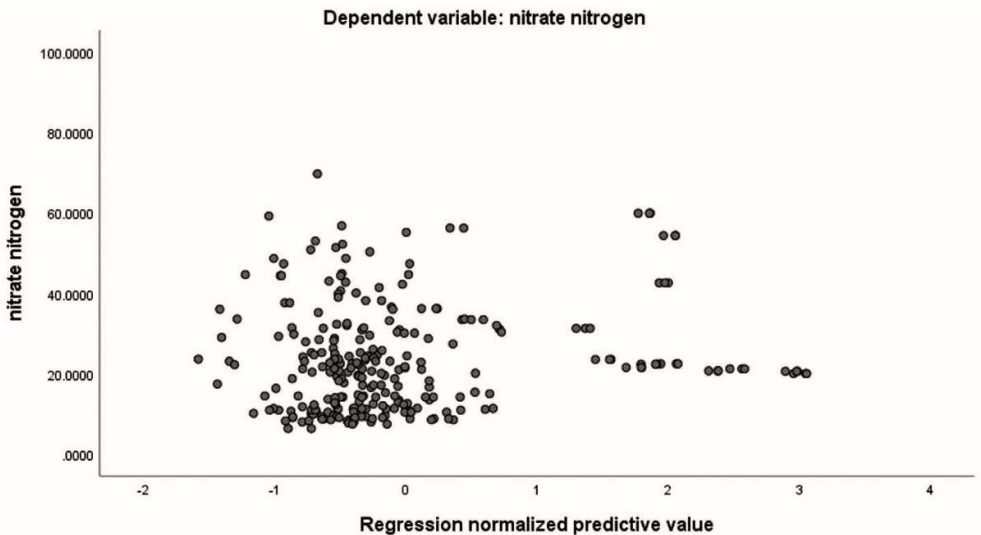


Figure 6. Scatter plot for nitrate nitrogen prediction.

Table 9. Multivariate analysis of variance of soil nitrate nitrogen in the *Picea mongolica* forest (T-Test).

model	Nonstandard Coefficient		Standardized number	t	Signifi- cance
	Beta		Beta		
particular year	13.24	47.05	0.10	0.28	0.078
Forest type	4.79	22.44	0.02	0.21	0.083
Soil depth	1.74	1.01	0.11	1.72	0.086
PH value	-39.97	41.03	-0.08	-0.97	0.331
humidity	54.79	15.91	0.41	3.44	0.001
temperature	-2.95	3.22	-0.14	-0.92	0.036
Litter N content	-30.05	122.53	-0.05	-0.25	0.081
Litter N content	-3.92	6.76	-0.45	-0.58	0.056
Litter CN ratio	12.71	23.19	0.54	0.55	0.058
Soil organic matter content	-0.29	0.27	-0.08	-1.06	0.029

From the linear fitting results in Table 5, humidity, temperature, and CN ratio of litter and organic matter have a considerable impact on the total N, and the highest contribution rate. The impact of litter N content and pH value is slightly lower, but the *p*-values for all other influencing factors, with the exception of litter N content, are greater than 0.05, indicating a significant result.

3.4. Correlation between soil total N, NH<sub>4</sub><sup>+</sup>—N, NO<sub>3</sub><sup>-</sup>—N content and month, soil depth and forest age

**Table 10.** Correlation coefficient between nitrogen stoichiometry in the soil of *Picea mongolica* forest and influencing factors \*at level 0.05 (two-tailed) with a significant correlation. \* \* At the 0.01 level (two-tailed), the correlation was significant.

	particular year	Soil depth	Forest type	total N	NNH4N	NNO3N	PH	tempera- ture	humidity	Litter C content	Litter N content	Litter C/N	Soil or- ganic matter content
particu- lar year	1	0	0	0.394**	0.11	0.44**	-0.164**	0.251**	0.258**	-0.957**	0.919**	-0.973**	0.052
Soil depth		1	0	-0.001	-0.228**	0.06	0.248**	-0.057	-0.165**	-0.76	-0.62	-0.71	-0.359**
Forest type			1	0.21	0.47**	0.006	-0.285**	0	-0.047	-0.196**	0.124*	-0.158**	0.166**
total N				1	0.037	-0.005	-0.029	0.078	0.008	-0.120*	0.093	-0.129*	0.066
NNH4N					1	-0.037	-0.222**	0.236**	0.388**	-0.002	-0.013	-0.005	0.264**
NNO3N						1	-0.140*	0.157**	0.265**	-0.038	0.024	-0.044	-0.012
PH							1	-0.246**	-0.413**	0.237**	-0.280**	0.229**	-0.531**
tempera- ture								1	0.819**	-0.185**	0.072	-0.266**	0.205**
humidity									1	-0.197**	0.130*	-0.255**	0.233**
Litter C content										1	-0.941**	0.993**	-0.086
Litter N content											1	-0.934**	0.119
Litter C/N												1	-0.085
Soil or- ganic matter content													1

The total soil N in the *Picea mongolica* forest has a positive correlation with the year, with a correlation coefficient of 0.394, a significant negative correlation with litter C content and litter CN ratio, with correlation coefficients of -0.120 and -0.129 respectively, and a positive correlation with ammonium N, temperature, humidity, litter N content, and soil organic matter content (Table 10). However, there is no significant correlation with soil depth, nitrate N, and pH value also showing a negative correlation. NH<sub>4</sub><sup>+</sup>—N had a significant negative correlation with soil depth and pH value, and the correlation coefficients were 0.228 and -0.222 respectively. There was a significant positive correlation with forest type, temperature, humidity, and soil organic matter content, and the correlation coefficients were 0.47, 0.236, 0.388, and 0.264 respectively. There was little positive correlation with years, but with nitrate N, litter C content, and litter N content, the litter CN rate showed a negative correlation. NO<sub>3</sub><sup>-</sup>—N had a positive correlation with year, temperature, and humidity, with clear significance. The correlation coefficients were 0.44, 0.157, and 0.265 respectively. There was a significant negative correlation with pH, with a correlation coefficient of -0.140. There was a weak positive correlation with soil depth, forest stand, and litter N content, and a weak negative correlation with total N, ammonium N, litter C content and litter CN rate.

4. Discussion

4.1. Effects of litter addition on the contents of total N, NH<sub>4</sub><sup>+</sup>—N and NO<sub>3</sub><sup>-</sup>—N in the soil of *Picea mongolica* forest

Forest litter is the main source of soil nutrients, and nutrients are returned to the soil following decomposition. This study found that there was a positive correlation between litter N content and soil organic matter, total N content, and NO<sub>3</sub><sup>-</sup>—N content across different forest ages. High N content in the litter and high soil organic matter, total N, and NO<sub>3</sub><sup>-</sup>—N contents were observed. There was a negative correlation between litter N and

$\text{NH}_4^+ - \text{N}$  contents. A negative correlation between litter C content and soil organic matter, total N, and  $\text{NO}_3^- - \text{N}$  contents was also observed. In this study, the total N and  $\text{NO}_3^- - \text{N}$  increased with the increase of N content during litter decomposition. The results are similar to those of different tree species studied by Pan et al. [4] and Magill et al. [15]. It is possible that N input increases the content of mineral N in the soil and litter layers, buffering the competition between plant absorption and nitrobacteria, as well as denitrifying bacteria for N, increasing nitrification and denitrification, and then increasing soil-available N [16]. This may also be related to the mineralization and fixation of N. The addition of N improves the soil nitrification process, resulting in more N in the form of  $\text{NO}_3^- - \text{N}$  [17]. As the increased N is absorbed by soil organic matter, C/N decreases, which improves the release rate of N during decomposition [18]. It is also possible that the added inorganic N is fixed by microorganisms, which promotes the mineralization and release of the original organic N [19].

#### 4.2. Effects of environmental factors on the contents of total N, $\text{NH}_4^+ - \text{N}$ and $\text{NO}_3^- - \text{N}$ the soil of *Picea mongolica* forest

The change in soil N content is affected by various environmental factors such as soil temperature, moisture, and pH. Differences in temperature, humidity, and litter supply in different niches affect N mineralization by influencing the number, species, and vitality of different microbial groups in the forest [18].

In this study, a positive correlation was observed between temperature and soil total N,  $\text{NH}_4^+ - \text{N}$ , and  $\text{NO}_3^- - \text{N}$ . The contents of total N,  $\text{NH}_4^+ - \text{N}$ , and  $\text{NO}_3^- - \text{N}$  increased with increasing temperature. This was similar to the research results of Zhao et al. [20]. The highest contents of total N,  $\text{NH}_4^+ - \text{N}$ , and  $\text{NO}_3^- - \text{N}$  on the soil surface of young, middle-aged, and near-mature forests were all recorded in July. This may be because the increase in temperature increases the availability of soil ammonia N and nitrate N, as the  $\text{NH}_4^+ - \text{N}$  of forest soil ammonification is the source of nitrification, with ammonification directly affecting the change in nitrification rate. The nitrification rate is often lower than the ammoniation rate [21]. The increase in temperature promotes the denitrification of the surface soil. In addition, when the temperature increases, the microbial growth and metabolism activity is enhanced and a large amount of organic matter is decomposed, which improves the mineralization rate of soil N and significantly increases the content of N in the soil [22]. Temperature change can also change the mineralization rate of N in the soil by affecting soil water content [21].

Soil moisture content is an important factor in the process of soil N transformation. In this study, the soil total N,  $\text{NH}_4^+ - \text{N}$ , and  $\text{NO}_3^- - \text{N}$  were positively correlated with soil moisture, and the contents of  $\text{NH}_4^+ - \text{N}$  and  $\text{NO}_3^- - \text{N}$  were significantly correlated with soil moisture. This may be because the joint action of soil water content and other soil physical and chemical properties can significantly alter the porosity and pore distribution of soil. This affects the circulation of oxygen in soil, which in turn affects the activity of microorganisms [23]. The short-term increase in temperature and water can significantly improve the activity of soil microorganisms, which is conducive to their growth and reproduction. This can change the contents of soil total N,  $\text{NH}_4^+ - \text{N}$ , and  $\text{NO}_3^- - \text{N}$ . As drought and low temperatures weaken biological activities, the litter decomposition rate decreases to a certain extent with low temperatures during winter (November) and during low precipitation (May).

Soil pH and other pH can directly or indirectly affect other properties and are the main variables affecting soils [24,25]. In this study, soil pH was negatively correlated with soil total N,  $\text{NH}_4^+ - \text{N}$ , and  $\text{NO}_3^- - \text{N}$ , as well as with  $\text{NH}_4^+ - \text{N}$  and  $\text{NO}_3^- - \text{N}$ . This is similar to the research results of Chen et al. [26]. Lower pH will limit the growth of soil denitrifying microorganisms. However, lower pH may reduce the availability of organic carbon and mineral N available to denitrifying microorganisms [27].

#### 4.3. Effects of seasonal variation on the contents of total N, $\text{NH}_4^+ - \text{N}$ and $\text{NO}_3^- - \text{N}$ in the soil of *Picea mongolica* forest

In the current study, the total N content of *Picea mongolica* forest across three different stand ages increased first and then decreased over time during 2017. The total N content for the three forest ages was the highest during May and July. This is because the N element mainly exists in the form of organic matter, and its release needs to be decomposed by microorganisms. In summer, microbial activity begins to increase, which promotes the decomposition of the N element [28]. The content of  $\text{NH}_4^+ - \text{N}$  across the three forest ages and in each soil layer is greater than that of  $\text{NO}_3^- - \text{N}$ , which is consistent with the research results of Zhao et al. [11]. This indicates that  $\text{NH}_4^+ - \text{N}$  is the main form of soil available n. Correlation analysis showed that seasonal dynamic changes had an effect on the  $\text{NH}_4^+ - \text{N}$  and  $\text{NO}_3^- - \text{N}$  in the *Picea mongolica* soil layer. The content was lower than in March and November, and higher during May and July. This is consistent with the results for two n elements in temperate forest soil studied by Xu et al. [3]. This may be because the weather warmed up during May, the snow melted, the soil temperature and humidity increased at the same time, the soil microbial activity began to increase, and the N mineralization, especially the ammoniation, increased [16]. This resulted in a large amount of decomposition of the N in the litter, and the contents of  $\text{NH}_4^+ - \text{N}$  and  $\text{NO}_3^- - \text{N}$  in sandy spruce soil for each forest age would have increased. The *Picea mongolica* then entered the growing season, and with the continuous increase of temperature, it needs to absorb a large amount of  $\text{NH}_4^+ - \text{N}$  [30,31]. Part of the  $\text{NH}_4^+ - \text{N}$  is transformed into  $\text{NO}_3^- - \text{N}$  through the action of nitrifying microorganisms. With the increase in rainfall,  $\text{NH}_4^+ - \text{N}$  and  $\text{NO}_3^- - \text{N}$  entered the deep soil layer through the leaching of rainwater. The  $\text{NH}_4^+ - \text{N}$  content then decreases to a certain extent. The high content during July was due to the slow growth of spruce on sandy land during autumn. The reduction in  $\text{NH}_4^+ - \text{N}$  absorption and its relative accumulation, is consistent with the results of  $\text{NH}_4^+ - \text{N}$  and  $\text{NO}_3^- - \text{N}$  in temperate forest soils studied by Xu et al. [3]. In November, the contents of  $\text{NH}_4^+ - \text{N}$  and  $\text{NO}_3^- - \text{N}$  in sandy spruce soils were 0–20 cm. The contents of the soil surface layer was greater than that at depths of 30–50 cm. The main reason for this is that the northern temperate zone enters winter in October, the weather is cold and the soil is covered with ice and snow. Low temperatures will inhibit the activities of soil microorganisms, weaken the humic effect and slow decomposition rates, which hinders the mineralization of soil [30].

#### 4.4. Effect of soil depth on the contents of total N, $\text{NH}_4^+ - \text{N}$ and $\text{NO}_3^- - \text{N}$ in the soil of *Picea mongolica* forest

Results showed that the total N,  $\text{NH}_4^+ - \text{N}$  and  $\text{NO}_3^- - \text{N}$  in *Picea mongolica* soils decreased with increasing soil depth (0–50 cm). There were significant differences between 0–10 cm, 10–20 cm, 20–30 cm, 30–40 cm, and 40–50 cm soil layers ( $p < 0.05$ ). This is consistent with trends in soil N content with increasing soil depth in forests in the Qinghai Province as well as the alpine forests in Western Sichuan [31,32]. This is because the process of decomposition and synthesis of litter returns n to the soil. On the soil surface, the N content mainly comes from litter decomposition. While litter is mainly concentrated on the soil surface, nutrients also accumulate there. Good ventilation and hydrothermal conditions on the soil surface provide a better environment for microbial activities, therefore promoting the accumulation of N content at the soil surface. Then the N migrates and diffuses down to the mineral soil layer with water or other media. In the deeper soil layers, the N content is mainly derived from roots, root exudates, soil microorganisms and N leaching from some of the upper layers. Compared with the soil surface layer, the exchange with the outside world is weak [33]. In addition, with the deepening of the soil layer, plant roots, soil animals and microorganisms absorb and utilize nutrients. As a result, the total N,  $\text{NH}_4^+ - \text{N}$  and  $\text{NO}_3^- - \text{N}$  in *Picea mongolica* soils decreased with the increase in soil depth (0–50 cm). This is consistent with the results of Qin et al. [34] on soil nutrients in different forest types with Masson pine (*Pinus massoniana* Siebold & Zucc.).

#### 4.5. Effects of forest age on the contents of total N, $\text{NH}_4^+ - \text{N}$ and $\text{NO}_3^- - \text{N}$ in the soil of *Picea mongolica* forest

This study has shown that the content of soil  $\text{NH}_4^+ - \text{N}$  during March and November 2017 was significantly different from that of May and August 2017 ( $p < 0.05$ ). The  $\text{NH}_4^+ - \text{N}$  content in the soil of the *Picea mongolica* forest generally showed a trend of near-mature forest > middle-aged forest > young forest. The trend in soil  $\text{NO}_3^- - \text{N}$  content is consistent with that of sandy spruce soil  $\text{NH}_4^+ - \text{N}$  content. This is similar to the results for different tree species studied by Pan et al. [4], Wang et al. [35] and Cui et al. [36]. This may be that during the growth of the *Picea mongolica* forest, the biomass gradually increased, the soil surface litter and animal and plant residues gradually increased, the soil texture has been greatly improved, and the number and variety of microorganisms are various and active. They decompose the soil surface litter and animal and plant residues, resulting in an increase in soil nutrients  $\text{NH}_4^+ - \text{N}$  and  $\text{NO}_3^- - \text{N}$  [4,37,38]. Due to the demand for N in different growth stages of *Picea mongolica*, the demand for soil N in young and middle-aged forest stages is high. After the forest has reached maturity, due to the slow and stable growth of *Picea mongolica*, the utilization rate of soil N may be lower. In addition, the deeper the soil has roots growing in the near-mature forest of *Picea mongolica*, the more conducive it is to the absorption of deep-seated soil nutrients. This also leads to the highest contents of  $\text{NH}_4^+ - \text{N}$  and  $\text{NO}_3^- - \text{N}$  at the soil surface when the forest reaches maturity [35].

The total N and ammonia N in the soils were found to be higher in the near-mature forest and middle-aged forest. In the young forest, it was found to be lower. This may be because plants at different growth stages have different nutrient needs, which can lead to differences in nutrient content in their own organs and litter [4].

## 5. Conclusions

(1) Total N and  $\text{NH}_4^+ - \text{N}$  in the soil of *Picea mongolica* forest were positively correlated with month, soil  $\text{NO}_3^- - \text{N}$  and forest age ( $p < 0.05$ ), and negatively correlated with soil depth ( $p < 0.01$ ).  $\text{NO}_3^- - \text{N}$  in *Picea mongolica* soil was negatively correlated with month and stand age ( $p < 0.05$ ), and significantly negatively correlated with soil depth ( $p < 0.01$ ).

(2) The  $\text{NH}_4^+ - \text{N}$  in each soil layer for *Picea mongolica* forest across the three forest ages is greater than that of  $\text{NO}_3^- - \text{N}$ . The correlation analysis shows that the seasonal dynamic change has an impact on the of soil  $\text{NH}_4^+ - \text{N}$  and  $\text{NO}_3^- - \text{N}$  contents of the *Picea mongolica* forest. The content was lower during February and November, and higher in May and August.

(3) The total N,  $\text{NH}_4^+ - \text{N}$ , and  $\text{NO}_3^- - \text{N}$  in sandy spruce soil for the three forest ages increased with the depth of the soil layer (0–50 cm) and showed an overall downward trend. Significant differences ( $p < 0.05$ ) in  $\text{NH}_4^+ - \text{N}$  content between 0–10 cm, 10–20 cm, 20–30 cm, 30–40 cm, and 40–50 cm soil layers in young forest were observed.  $\text{NO}_3^- - \text{N}$  content also showed a significant difference ( $p < 0.05$ ), but there was no significant difference in  $\text{NH}_4^+ - \text{N}$  content between middle-aged forest and near-mature forest with increasing soil depth.

(4) The content of N,  $\text{NH}_4^+ - \text{N}$  in the soil of the *Picea mongolica* forest generally showed a trend of near-mature forest > middle-aged forest > young forest. The trend for soil  $\text{NO}_3^- - \text{N}$  content is consistent with that of  $\text{NH}_4^+ - \text{N}$  content in the soil of *Picea mongolica* forest.

**Supplementary Materials:** The following supporting information can be downloaded at: [www.mdpi.com/xxx/s1](http://www.mdpi.com/xxx/s1), Table S1: Key vegetation parameters of the sampling plots; Table S2: Mean air temperature and precipitation in different months; **Table S3.** Soil ammonium nitrogen and nitrate nitrogen contents and their vertical distribution in different stand ages and times in young forest (Y-F); middle-aged forest (M-F); and near-mature forest (N-F).



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