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Effect of Simulated Combined N and P on Soil Acidity within Soil Aggregates in Natural and Planted Korean Pine Forest in Northeast China

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Abstract: Globally, atmospheric nitrogen (N) deposition is rising, adversely impacting soil health, i.e., increasing soil acidity. While phosphorus (P) is the limiting element in the temperate environment and plays a key role in making the ecosystem more vulnerable to N-derived acidification. The impact of elevated N and P inputs on soil acidity and exchangeable base cations have been extensively studied; however, few studies have focused on these parameters, especially within various soil aggregate fractions in the temperate forest. In 2017, a field experiment was conducted under N and P additions with four soil aggregate fractions (>5 mm, 2–5 mm, 0.25–2 mm, and <0.25 mm) in two forests, i.e., the broad leave Korean pine forest (BKPF) and Korean pine plantation (KPP) in the Liangshui National Natural Reserves in Northeast China. Results showed that high NP addition decreases pH, base cations, Mg^{2+} Ca^{2+}, and BS% and increases in Fe^{3+}, Al^{3+}, and E.A (effective acidity) in all four aggregate fractions, in descending order; overall concentration of the base cations is ranked as BKPF > KPP. Thus, soil acidification is primarily caused by a decrease in base cations, such as Ca^{2+} and Mg^{2+}, and increase in exchangeable Fe^{3+} and Al^{3+} ions in large macro-aggregates and macro-aggregates, which leads to the depletion of soil nutrients. The initial pH value (5.69) in >5 mm soil aggregate was decreased to (5.4) under high fertilizer application, while a minimum value of 5.36 was observed in 0.25–2 mm aggregates under high fertilizer application. The same trend was observed in all aggregates because of decrease in base cations, which, in turn, affects the vitality and health of the forests.

Keywords: acidity; fertilization; aggregates; fertility; nutrition; ecosystem

1. Introduction

Nitrogen (N) and phosphorus (P), two essential macronutrients, constrain the primary productivity across the terrestrial ecosystem [1,2]. External N inputs to the terrestrial ecosystem are controlled by nitrogen fixation and atmospheric deposition. P availability is controlled by mineral weathering and atmospheric deposition [2]. The demand for mineral nutrients by trees may be brought about by all of the biogeochemical processes above, leading to a soil nutrient imbalance [3]. Phosphorus (P) remains an important, yet ubiquitous, nutrient limitation in different ecosystems [4] and is a necessary ingredient for growth and development in organisms [5]. The P cycling of soil in diverse ecosystems is, thus, considered an essential factor [2]. In general, N is regarded as a nutrient that limits forest development [6], particularly in temperate forests where soil is relatively young [7]. The acidification of forest soil is a natural process and one of the most severe environmental issues in Europe, Asia, and other parts of the globe; in many temperate and boreal regions, soil acidification is regarded as a significant ecological issue [8]. Soil acidity occurs for two main reasons: first, natural weathering, plant nutrient uptakes, or microorganism activities; second, and most important, is anthropogenic activities, such as fertilization, especially nitrogen, which play a vital role, along with different bases cations and phosphorus [9]. The N inputs promote soil acidification and cause the loss of base cations [10], and bioavailability of micronutrients may increase under soil acidification [11]. The N addition causes exchangeable Ca^{2+} and Mg leaching, and that activates available Fe^{3+} and Mn^{2+}. As a result, soil acidification occurs, which leads to the imbalance of nutrients in the soil [10]. On the other hand, increasing N deposition may enhance forest development, while limiting other nutrients, such as phosphorus (P) and base cations [12]. The loss of nutrients (K^{+}, Ca^{2+}, Mn^{2+}, and Mg^{2+}), due to canopy leaching [13,14], which is due to precipitation and throughfall, may change the chemical characteristics of the soil water, modifying soil acidity, Ca:Al ratio, alkalinity, acid neutralizing capacity, and saturation of base cations [13,15,16].

Tree species composition may influence soil acidity and exchangeable cations concentration in soil development [17,18]. Plant communities are intimately related to the ground and below-ground processes [19]. Global changes may substantially affect the diversity and composition of plants [20], and large areas of mixed broad-leaved Korean pine (*Pinus koraiensis*) forest have been harvested and converted into secondary forest and plantations during the past several decades [21]. The worldwide data show that, by 2050, the rate of N deposition will be twice that of 1995, which was 100 Tg N a^{-1} to 200 Tg N a^{-1}, respectively [22]. Similarly, from 1990 to 2000, China's averages wet-N deposition rate rose to 25% [23] and is anticipated to grow dramatically in the future. Northern China was discovered to be one of the deposition sites for N in Asia, with a range from 28.5 to 100.4 N ha^{-1} a^{-1} [24].

The biogeochemical cycles of N and P are strongly linked [25,26], and the processes of N and P are closely connected. In some cases, N was shown to have expanded the limits of P [27]. In others, N addition has performed the P dynamics and increased P cycling [28,29]. Researchers worldwide have been paying great attention to carbon (C) cycling with increased deposition of N [30–32]. However, the P dynamics, base cations, Al:Ca ratio, and microbial and enzyme activity, under increasing N exposures, have received less attention because these are excellent eco-chemical markers for the health of the soil and damages occurred by soil acidification [33]. The fundamental unit of soil structure is the aggregates, which provide an important indicator of soil health by predicting the characteristics and distribution of microbes and enzymatic communities and other soil nutrients, such as phosphorus, sulfur, and nitrogen, among others [34]. Soil aggregates are formed by repeated polymerization of organic and inorganic colloid, which determines the distribution of microbial community and nutrients. Soil aggregate stability serves as an important indicator of soil health [35,36]. Aggregation of soil is physical protection connected with soil organic matter (SOM) stabilization. Water diffusion and oxygen rate are generally similar with soil aggregate sizes and determined by pore spaces [37]. As a result, N and P are more likely to distribute in aggregates of larger sizes because of favorable microbial activity [38]. High mineral content and more microbial-processed SOM with micro aggregates [39].

This study provides the effect of simulated N and P deposition/fertilization on soil acidification and base cation depletion in different aggregate sizes in the temperate ecosystems. We hypothesized that different levels of combined N and P fertilization would: (1) increase acidification and changes in base cation concentration within soil aggregates; and (2) affect eco-chemical indexes, such as effective acidity (EA), base saturation, Al:Ca ratio, and soil pH in different soil aggregates.

2. Materials and Methods

2.1. Study Site

The study site is located at the Liangshui National Nature Reserve, at position (47°6′49″–47°16′10″ N, 128°47′8″–128°57′19″ E) of the Mountains Xiao Xing′an, in the Heilongjiang Province of northeastern China. The region is characterized by a temperate climate with a mean annual temperature of −0.3 °C (i.e., min. −31 °C in Jan and max. 32 °C in July). The total mean annual precipitation in the region was recorded as 676 mm, and 60% of the annual precipitation occurs during the growing season from June to August. The frost-free period is from 100 to 120 days, and the accumulated snow period is from 130 to 150 days. The reserve covers 12,133 hm^2, with an approximate growing stock of 1.88 million m^3 and average canopy coverage of 98%. The study area is one of the prime areas in China that have a huge natural forest. Among these forests, 2375 hm^2 area is covered with natural Korean pine forests. The climate is a continental monsoon with a strong monsoon windy spring, warm and humid summer, and dry and cold winter. The ambient N deposition in the region is 12.93 kg N hm^2 a^{-1}. The study site is dark brown forest soil classified as Inceptisols (USDA Soil Taxonomy) and Bori-Udic Cambosol (Chinese Soil Taxonomy). Bori-Udic Cambosols mainly distribute in China's northeast areas, including the Greater Khingan, Lesser Khingan, Wanda, and Changbai Mountains. Parent materials are diversified, including the weathered materials derived from granite, gneiss, sandstone, shale, and limestone, as well as loess. The main tree species is the Korean pine (*Pinus koraiensis)*, accompanied by temperate deciduous tree species, (Table 1) such as *Betula costata*, *Tilia amurensis*, *Acer ukurunduense Abies nephrolepis*, *Ulmus laciniata*, *Acer tegmentosum*, and *Fraxinus mandshurica.* See Table 2 for soil characteristics before fertilizer application.

Table 1. Summary of the mixed broad-leaved Korean pine forest (BKPF) and planted Korean pine plantation (KPP).

Site Characteristics of Forest Stands							
Forest Stand / Forest Type	Main Species Composition	Land Use History	Age (Year)	Stand Density (Trees/hm^{-2})	Mean DBH (cm)	Canopy Closure	Soil Density (g/m^{-3})
Broad-leaved Korean pine forest (BKPF)	*Pinus koraiensis*, *Betula costata*, *Tilia amurensis*, *Acer ukurunduense*, *Abies nephrolepis*, *Ulmus laciniata*, *Acer tegmentosum*, and *Fraxinus Mandshurica*	Natural forest	>230	1175	21.1	0.75	0.99
Planted Korean pine plantation (KPP)	*Pinus koraiensis*	Reforestation in 1954 after clear-cutting of primary mixed broad-leaved Korean pine forest	65	1475	26.4	0.7	0.80

Table 2. Summary of soil chemical properties in different soil aggregates before applying fertilizers.

	Soil Aggregates (mm)									
	Bulk Soil		>5 mm		2–5 mm		0.25–2 mm		>0.25 mm	
	BKP	KPP	BKPF	KPP	BKPF	KPP	BKPF	KPP	BKPF	KPP
pH	5.70	5.65	5.65	5.61	5.57	5.60	5.60	5.58	5.72	5.61
SOC (g kg^{-1})	63.2	60.3	59.23	57.3	55.4	52.54	48.4	46.5	44.4	42.3
AP (mg $kg^{-1)}$	40.2	36.2	24.20	21.5	22.3	20.10	15.2	14.1	13.5	13.0
TN (g kg^{-1})	4.70	4.10	3.50	3.30	2.90	2.50	2.50	2.30	1.90	1.80
TP (g kg^{-1})	3.10	2.90	2.10	1.90	1.60	1.45	1.76	1.35	1.20	1.05
C:N (ratio)	13.4	14.7	16.9	17.3	19.1	21.01	19.3	20.2	23.3	23.5
NH_4–N (mg kg^{-1})	40.6	38.2	36.8	34.2	34.1	33.06	24.5	23.1	24.3	22.4
NO_3–N (mg kg^{-1})	6.40	5.30	7.43	6.20	6.50	6.10	4.20	3.90	3.80	3.60

2.2. Experimental Design

In October 2017, three sample plot of 20 × 20 m was set up in each of the two representative forest types, i.e., broad-leaved Korean pine forest (BKPF) and Korean pine plantation (KPP), with similar site conditions. Then, each sample plot was subdivided in to twelve (2 × 2 m) subplots, and an additional 20 m buffer zone was established between two adjacent sample plots, as well as around the edges of the plots, in order to reduce mutual interference. Thus, a total of 72 subplots were established in both forest types. In 2018 and 2019, the following four levels of fertilization were implemented: control (CK, 0 g N m^{-2} a^{-1}, and 0 g P m^{-2} a^{-1}), low fertilization (N_1P_1, 5 g N m^{-2} a^{-1}, and 5 g P m^{-2} a^{-1}), medium fertilization (N_2P_2, 15 g N m^{-2} a^{-1}, and 10 g P m^{-2} a^{-1}), and high fertilization (N_3P_3, 30 g N m^{-2} a^{-1}, and 20 g P m^{-2} a^{-1}). Ammonium sulphate ($(NH_4)_2SO_4$) was used as a nitrogen source, while ammonium phosphate ($(NH_4)_2HPO_4$) was used as a phosphorus source; both N and P were dissolved in water, and a 2 L sprinkler was used to simulate nitrogen and phosphorus deposition and sprayed by artificial sprayer. The rate of nitrogen and phosphorus treatment were set on the basis of local summer rainfall records and determination of natural NP settlement in the region (i.e., 12.93 kg ha^{-1} a^{-1}), based on the background values of natural nitrogen and phosphorus settlement and reference to similar international research methods [39,40].

2.3. Soil Sampling and Processing

Soil samples were collected in October 2019, at 0–20 cm soil depth, three randomly selected sampling points from each subplot were mixed into a composite sample, packed in the plastic bags, and transported to the laboratory. In the lab, all the soil samples were is air-dried and roots and stones are removed by hand. After that, the different soil aggregates sizes >5 mm, 2–5 mm, 0.25–2 mm, and <0.25 mm were separated via wet sieving procedure and put in the oven at 105 °C for further chemical analysis.

2.4. Chemical Analysis

Exchangeable cations (H^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+}) were extracted with 0.1 mol L^{-1} $BaCl_2$ (50:1, solution: soil). After centrifugation and filtration through 0.45 µm cellulose–acetate filters, the filtrates were analyzed for cations. Exchangeable H^+ and Al^{3+} were determined by NaOH neutralization titration after $BaCl_2$ extraction. The soil organic carbon and total nitrogen were determined using the dry combustion method, using the Vario EL III elemental analyzer (Elementar analyzer system GmbH, Hanau, Germany). The NH^{4+}-N (ammonium) and NO^3–N (nitrate) were obtained using 2 M KCl as determined by auto analyzer III Bran + Luebbe GmbH, Germany. Aluminum (Al) and iron (Fe) were taken out, using the method of [41], and the sample was examined through a machine, identified as coupled plasma mass spectrometry (Agilent Technologies Co. Ltd, CA, USA). For the determination of soil pH, 1 g soil was mixed with distilled water, in the ratio (1:2.5), and shaken on a mechanical shaker (30 min); the soil pH was measured using the calibrated pH meter (Mettler Toledo Seven Compact, Tokyo Japan).

2.5. Effective Cation Exchange Capacity, Base Saturation%, Al:Ca Ratio, and Effective Acidity Calculated by the Following Formula

The soil effective cation exchange capacity (ECEC) was calculated by adding all the exchangeable base cations on an equivalent basis. The fractions of base cations, such as K^+, Na^+, Ca^{2+}, and Mg^{2+}, in ECEC were calculated as the base saturation, while the effective acidity was measured by combining exchangeable aluminum and hydrogen ions [42]. The calculations are as given below:

$$\text{ECEC (cmolkg}^{-1}) = K^+ + Na^+ + Mg^{2+} + Ca^{2+} + Mn^{2+} + Fe^{3+} + Al^{3+} + H^+ \text{ (add on equivalent basis).}$$

$$\text{BS\%} = (K^+ + Na^+ + Mg^{2+} + Ca^{2+})/\text{CEC} \times 100$$

$$\text{Al:Ca} = Al^{3+}/Ca^{2+}$$

$$\text{E.A (cmolkg}^{-1}) = Al^{3+} + H^+$$

3. Statistical Analysis

ANOVA of factorial design for forest types, fertilization, soil aggregates, and their interactions were carried out to examine whether the N and P fertilizers affected the exchangeable cations or otherwise. The Shapiro–Wilk test was used to check the normality, while the post-hoc Tukey honest significant difference (HSD) test was applied to compare treatments (Table 3). The heatmap for Pearson's correlation coefficients was performed, in order to determine positive or negative correlations within soil chemical properties. Pearson's correlation analysis was performed with the "corrplot" package in "R", v. 3.6.1 [40]. A redundancy analysis (RDA) was used to identify the soil properties (i.e., soil acidity) that predicted the variations in the base cations. The RDA was performed with the "rda" function by using the "vegan" package in R, v. 3.6.1 [41–43]. All statistical analyses were performed in the program R, v. 3.6.1 [42]. SigmaPlot v. 12.5 (Systat Software Inc., San Jose, CA, USA) was used for graphical representations. Mean data were displayed as mean ± SE. If not noted otherwise, a significance level was reported at 0.05.

Table 3. Two-way ANOVA results of forest types, soil aggregates, fertilization, and their interactions on the soil chemical properties, in three replications of the broad-leaved Korean pine forest and Korean pine plantations at four combined (NP) levels of fertilization (CK, 0 g N, and P.), low (5 g N m^{-2} a^{-1} 1; 5 g P m^{-2} a^{-1}), medium (15 g N m^{-2} a^{-1} + 10 g P m^{-2} a^{-1}), and high (30 g N m^{-2} a^{-1}; 20 g P g m^{-2} a^{-1}) in Northeast China.

Source of Variations	**df**	**pH**	**SOC**	**C/N**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**Na^+**	**Al^{3+}**	**H^+**	**Fe^{3+}**	**Mn^{2+}**
Forest types (FT)	1	0.799	0.204	0.153	0.009	0.001	0.127	0.184	0.001	0.001	0.316	0.027
Soil aggregates (SA)	3	0.385	0.001	0.066	0.010	0.001	0.422	0.509	0.203	0.001	0.004	0.001
Fertilization (Fert)	3	0.001	0.001	0.295	0.137	0.001	0.008	0.896	0.002	0.001	0.001	0.081
FT × SA	3	0.997	0.998	0.992	0.966	0.131	0.907	1.000	0.997	0.508	0.944	0.997
FT × Fert	3	1.000	0.998	1.000	1.000	0.778	0.893	1.000	0.845	0.965	0.900	1.000
SA × Fert	9	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.999	1.000	1.000
FT × SA × Fert	9	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Source of variations	df	Ap	NO_3	NH_4	TP	Al:Ca	ECEC	BS %	E.A	TN	Proportion %	
Forest types (FT)	1	0.933	0.001	0.108	0.039	0.001	0.001	0.833	0.001	0.196	0.397	
Soil aggregates (SA)	3	0.018	0.169	0.001	0.003	0.001	0.001	0.002	0.001	0.529	0.001	
Fertilization (Fert)	3	0.039	0.001	0.449	0.163	0.001	0.085	0.001	0.001	0.911	0.956	
FT × SA	3	0.966	0.943	0.928	0.994	0.791	0.288	0.255	0.561	1.000	0.105	
FT × Fert	3	0.935	0.881	1.000	1.000	0.281	0.918	0.998	0.841	1.000	0.955	
SA × Fert	9	1.000	0.998	1.000	1.000	0.99	1.000	0.999	0.990	1.000	0.826	
FT × SA × Fert	9	1.000	1.000	1.000	1.000	0.999	1.000	1.000	1.000	1.000	0.976	

4. Results

4.1. Impact of Simulated Nitrogen and Phosphorus Deposition on Soil Properties

Soil chemical properties were significantly affected by fertilization levels and soil aggregates across both forest types. The base cations, i.e., the Ca^{2+} and Mg^{2+} ions, were significantly decreased with the increase in fertilizer levels. Ca^{2+} ions decreased from 25 to 22 (>5 mm), 22 to 19 (2–5 mm), 20 to 18 (0.25–2 mm), and 27 to 23 (<0.25 mm) in BKPF. The overall observed amounts of Ca^{2+} ions in KPP were comparatively less to BKPF; however, the decreasing trend under high fertilization was similar. The overall results are depicted in Figure 1. Similarly, Mg^{2+} ions decreased with the increase in NP application quantities. The highest value was observed in the control plot, as 2.62 (<0.25 mm), which was decreased to 2.42 under high fertilization in BKPF, while the minimum value of 2.17 (>5 mm) was observed in the high fertilization treatment in KPP. The overall detailed results are depicted in Figure 1, while Mn^{2+} Na^+ and K^+ remained constant under medium and high fertilization, across all soil aggregates and both forests. In contrast, the effective acidity (Al^{3+} and H^+) and Fe^{3+} significantly increased under medium and high fertilization, across all soil aggregates, relative to control and low fertilization. Al^{3+} ions were initially observed as 4.99 in the control plots, which increased to 5.72 in macro-aggregates, while its value increased from 5.09 in the control to 5.48 in (<0.25 mm) under high fertilization in KPP.

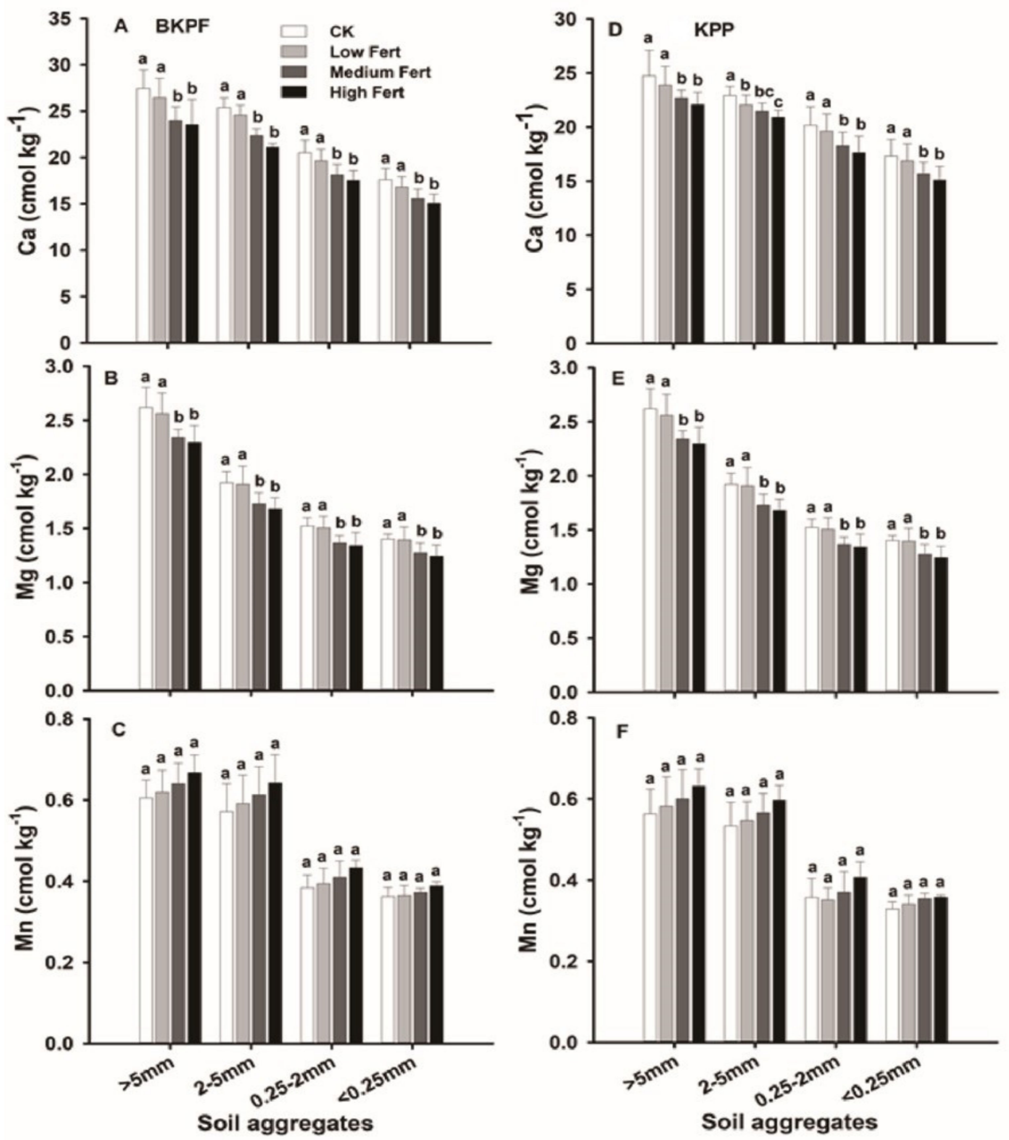

Figure 1. Calcium (Ca^{2+}) (cmol kg^{-1}) (**A**,**D**), magnesium (Mg^{2+}) (cmol kg^{-1}) (**B**,**E**), and manganese ion (Mn^{2+}) (cmol kg^{-1}) (**C**,**F**) at the control (C: no additional deposition; white bars) and after low NP: 05-g N m^{-2} a^{-1} + 05-g N m^{-2} a^{-1}; light grey, medium NP: 15-g N m^{-2} a^{-1} + 10-g N m^{-2} a^{-1}; dark grey, and high NP: 30-g N m^{-2} a^{-1} + 20-g N m^{-2} a^{-1}; black fertilization in respective soil aggregates >5 mm, 2–5 mm, 0.25–2 mm, and <0.25 in three replications at 0–20 cm soil depth of broad-leaved Korean pine forest (BKPF) and Korean pine forest (KPP) in Northeast (NE) China. Significant differences between treatments are indicated by different lower-case letters (Tukey's HSD post hoc; $p < 0.05$; mean ± SE).

The similar increasing trend was present in KPP as depicted in Figure 2. Soil pH significantly decreased by medium and high fertilization in all soil aggregates across both forest types. The initial pH and other ions were determined, and the results are depicted in Figure 2. After fertilizer application the soil pH decreased, i.e., a value of 5.69 was observed initially in >5 mm aggregate, which decreased to 54 under high fertilizer in BKPF.

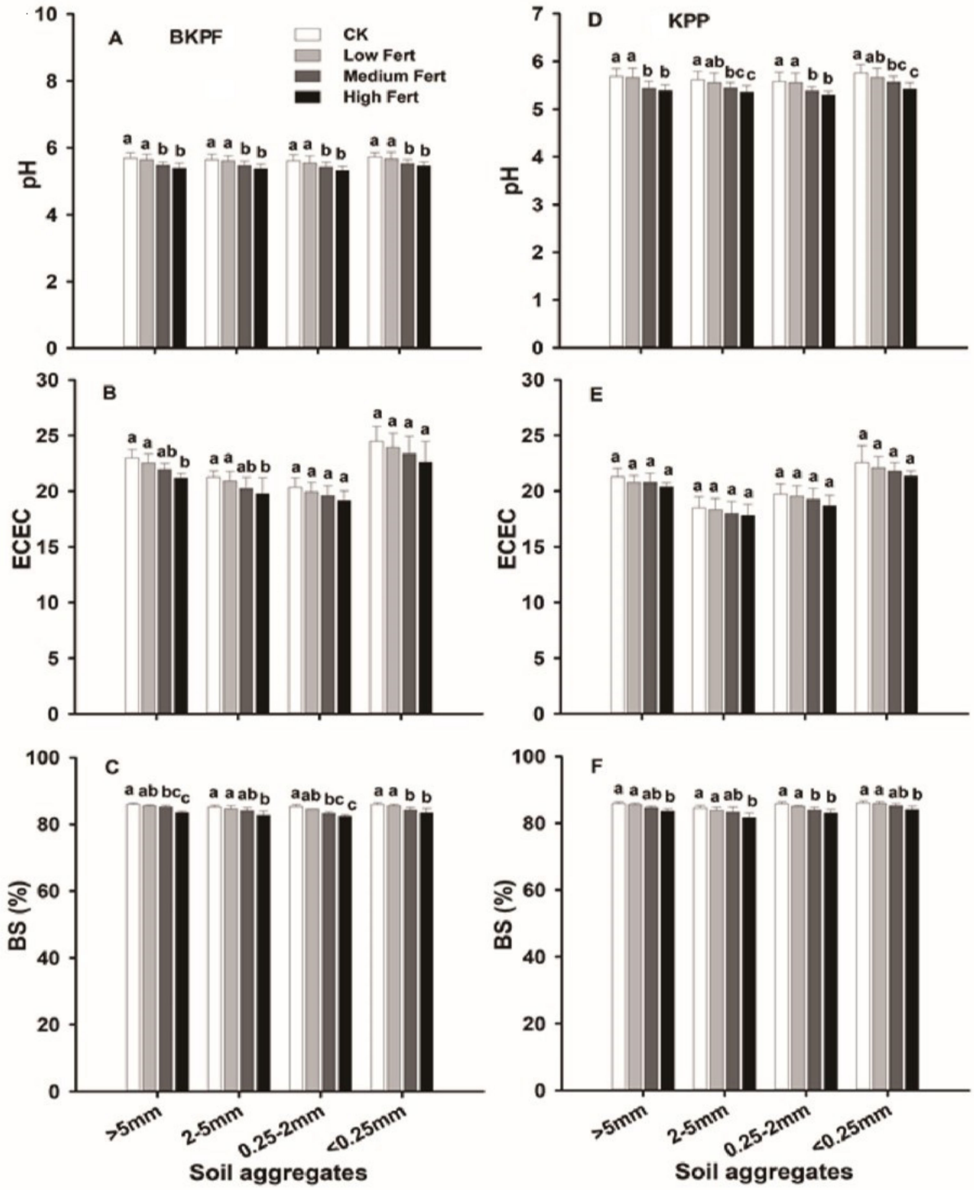

Figure 2. Soil pH (pH) (**A**,**D**), effective cation exchange capacity (ECEC) (**B**,**E**), and base saturation percentage (BS%) (**C**,**F**) at the control (C: no additional deposition; white bars) and after low NP: 05-g N m^{-2} a^{-1} + 05-g N m^{-2} a^{-1}; light grey, medium NP: 15-g N m^{-2} a^{-1} + 10-g N m^{-2} a^{-1}; dark grey, and high NP: 30-g N m^{-2} a^{-1} + 20-g N m^{-2} a^{-1}; black fertilization in respective soil aggregates >5 mm, 2–5 mm, 0.25–2 mm, and <0.25 in three replications at 0–20 cm soil depth of mixed broad-leaved Korean pine forest (BKPF) and artificial Korean pine forest (KPP) in Northeast (NE) China. Significant differences between treatments are indicated by different lower-case letters (Tukey's HSD post hoc; $p < 0.05$; mean $\pm$ SE).

The same decreasing trend was observed in all aggregates. In KPP soil, pH was observed as 5.42 under high dose (>5 mm), while a value of 5.36 (5.2 mm) was observed in high dose. The detailed values are depicted in Figure 2. In contrast, soil was not significantly affected by soil aggregates and forest types. We observed that BKPF forest type performed better than KPP forest (BKPF > KPP) (Figure 1). NO_3–N and soil organic C significantly increased, while AP significantly decreased with fertilization across both forests. In contrast, total N, ammonium N (Figure 3), total phosphorus, and C:N did not significantly affect fertilization across all soil aggregates across both forests. While the effects of low fertilization remained stable.

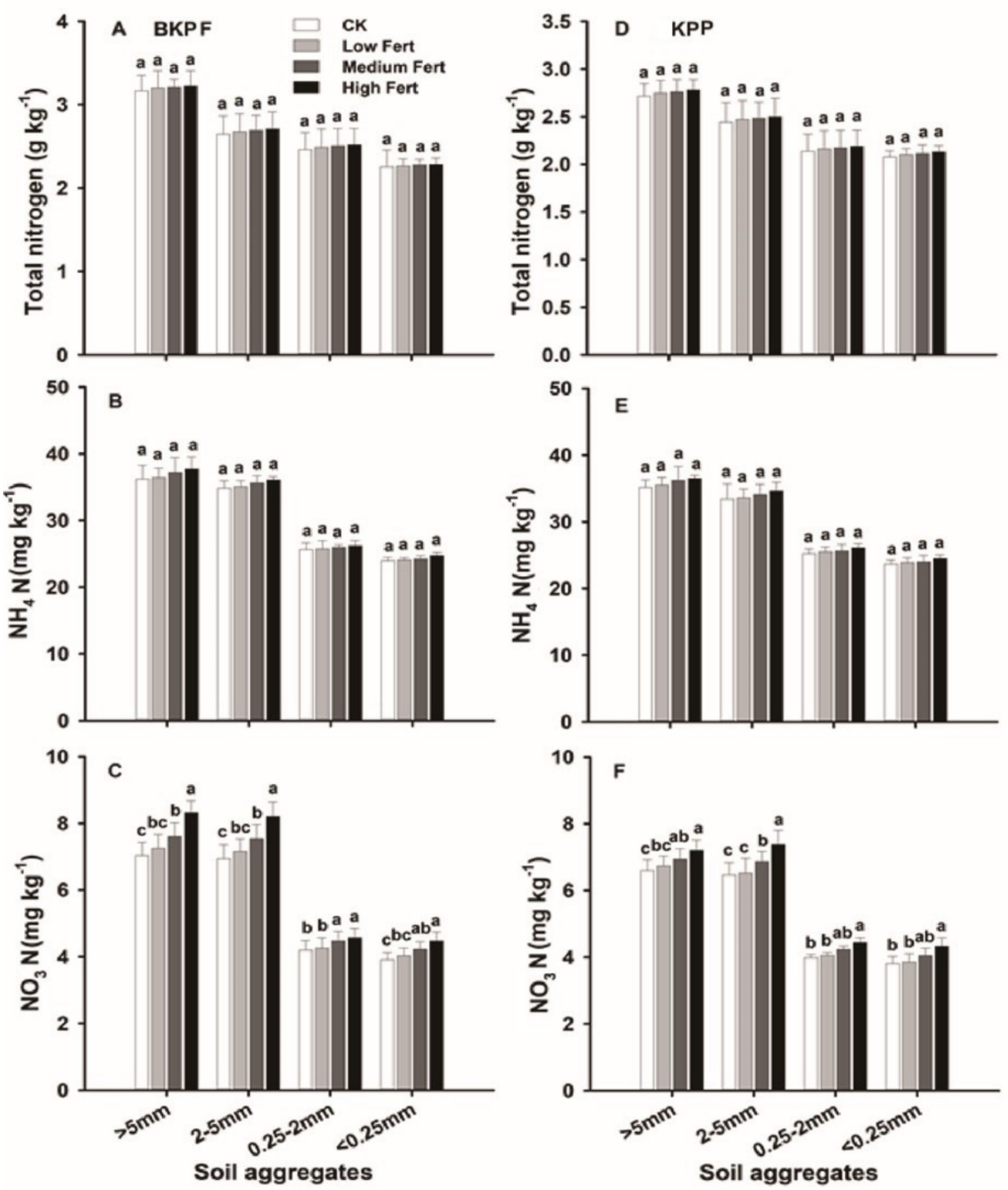

Figure 3. Total nitrogen (**A**,**D**), NH_4-N (mg kg^{-1})(**B**,**E**), and NO_3-N (mg kg^{-1}) (**C**,**F**) at the control (C: no additional deposition; white bars) and after low NP: 05-g N m^{-2} a^{-1} + 05-g N m^{-2} a^{-1}; light grey, medium NP: 15-g N m^{-2} a^{-1} + 10-g N m^{-2} a^{-1}; dark grey, and high NP: 30-g N m^{-2} a^{-1} + 20-g N m^{-2} a^{-1}; black fertilization in respective soil aggregates >5 mm, 2–5 mm, 0.25–2 mm, and <0.25 in three replications at 0–20 cm soil depth of mixed broad-leaved Korean pine forest (BKPF) and artificial Korean pine forest (KPP) in Northeast (NE) China. Significant differences between treatments are indicated by different lower-case letters (Tukey's HSD post hoc; $p < 0.05$; mean ± SE).

4.2. Impact of Soil Aggregates on Soil Properties

While Ca^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+}, H^+, and Fe^{3+} were significantly varied across all soil aggregates, and the greatest concentrations were observed in large macro-aggregates (i.e., >5 mm) as 25.4, 2.53, 0.61, 4.99, 0.60, and 2.8, respectively, under control plots. Ca^{2+} ion decreased with decrease in soil aggregate size. The similar situation was observed for Mg^{2+} (Figure 1) the least concentrations were observed in small micro-aggregates (i.e., <0.25 mm). In contrast, the Na^+, Mg^+, and soil pH remained constant, while Al^{3+} decreased (but not significant) across all soil aggregates in both forests (Table 4). Soil organic C, NH_4–N, TP, and C:N significantly decreased, while AP significantly increased by soil aggregates. However, the impact of soil aggregates on total N and NO_3–N remained constant (Figure 3). The Al: Ca ratio and proportion percentage significantly decreased by soil aggregates. While impact of soil aggregates on ECEC was not consistent, ECEC significantly decreased in aggregates >5 mm to <0.25–2 mm and increased in <0.25 mm.

Table 4. Aluminium ion (Al^{3+}) (cmol kg^{-1}) hydrogen ion (H^+) (cmol kg^{-1}) and iron ion (Fe^{3+}) (cmol kg^{-1}) at the control (C), low NP: 05-g N m^{-2} a^{-1} + 05-g N m^{-2} a^{-1}; medium NP: 15-g N m^{-2} a^{-1} + 10-g N m^{-2} a^{-1}; and high NP: 30-g N m^{-2} a^{-1} + 20-g N m^{-2} a^{-1}; fertilization in respective soil aggregates >5 mm, 2–5 mm, 0.25–2 mm, and <0.25 in three replications at 0–20 cm soil depth of mixed broad-leaved Korean pine forest (BKPF) and Korean pine forest (KPP) in Northeast (NE) China.

Aggregate Size	Al^{3+} (cmol kg^{-1})				H^+ (cmol kg^{-1})				Fe^{3+} (cmol kg^{-1})			
	C	Low NP	Medium NP	High NP	C	Low NP	Medium NP	High NP	C	Low NP	Medium NP	High NP
						BKFP						
>5 mm	4.99	5.11	5.51	5.72	0.64	0.66	0.68	0.72	2.91	3.01	3.26	3.37
2–5 mm	4.72	4.78	5.43	5.60	0.53	0.56	0.58	0.61	2.77	2.70	3.19	3.32
0.25–2 mm	3.39	3.43	3.62	3.65	0.38	0.40	0.42	0.45	2.35	2.30	2.57	2.67
<0.25 mm	3.02	3.18	3.52	3.58	0.32	0.33	0.35	0.38	2.14	2.09	2.33	2.43
						KPP						
>5 mm	4.36	4.47	4.73	4.88	0.59	0.60	0.61	0.64	2.8	2.9	3.1	3.2
2–5 mm	4.15	4.19	4.58	4.64	0.48	0.48	0.52	0.55	2.7	2.8	3.0	3.1
0.25–2 mm	2.95	2.97	3.13	3.21	0.36	0.37	0.39	0.41	2.3	2.4	2.6	2.7
<0.25 mm	2.75	2.77	2.97	3.02	0.30	0.31	0.32	0.34	2.1	2.2	2.4	2.5

4.3. Correlation of Soil Properties

The trait interrelations, across forest types, i.e., BKPF (A) and KPP (B); soil pH was found to be significantly negatively correlated to SOC, Al, and Fe, while significantly positively correlated to Mg^{2+} and BS% in BKPF, as well as significantly positively correlated to TP and ECEC in KPP (Figure 4B). SOC was significantly negatively correlated to Mg in BKPF and significantly positively correlated to NO_3 in KPP. K was significantly positively correlated to Al^{3+}, H^+, AP, NO_3–N, and NH_4–N, while significantly negatively correlated to Fe in KPP. Ca^{2+} was significantly positively correlated to Mg^{2+} and Al^{3+} in KPP. Mg was significantly negatively correlated to Na^+ and TN in KPP. Na^+ was significantly negatively correlated to Fe in BKPF. Al^{3+} was significantly positively correlated to Fe^{3+} and NO_3–N in BKPF, while significantly positively correlated to NH_4–N in KPP. H^+ was significantly positively correlated to Fe in BKPF, while significantly positively correlated to NH_4–N in KPP. Fe was significantly positively correlated to NO_3–N and NH_4–N in BKPF, while significantly positively correlated to TN in KPP. Mn^{2+} was significantly negatively correlated to AP, while significantly positively correlated to NO_3–N in KPP. AP was significantly positively correlated to NH_4–N in KPP. NO_3–N was significantly negatively correlated to BS in BKPF. NH_4–N was significantly positively correlated to ECEC in KPP. ECEC was significantly negatively correlated to TN in BKPF. BS was significantly negatively correlated to TN in KPP (Figure 4B).

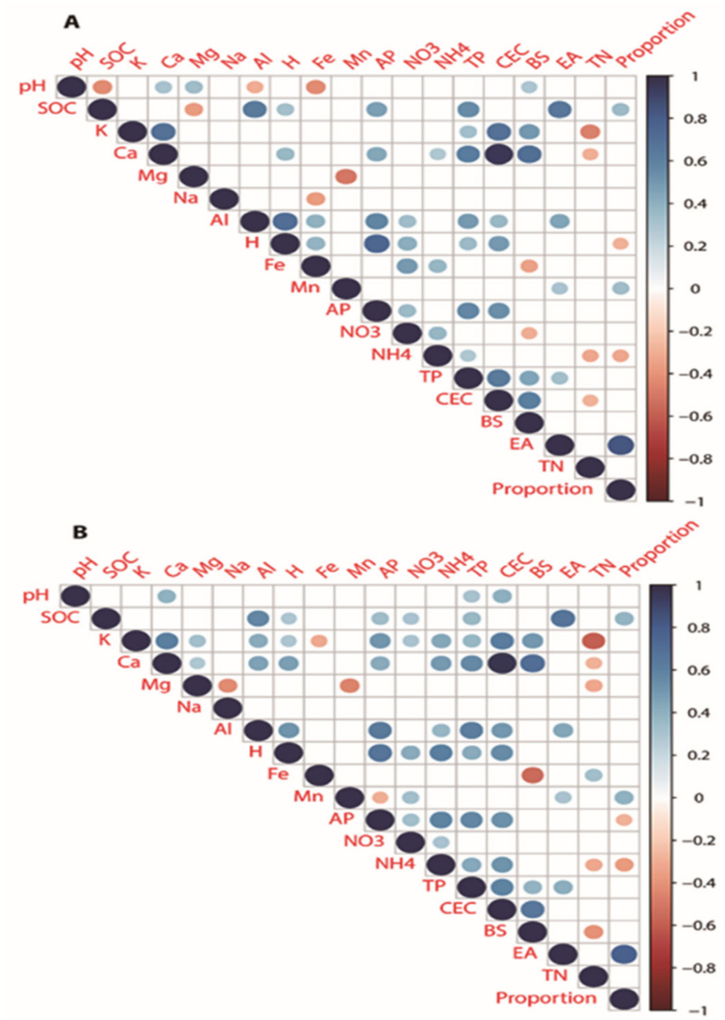

Figure 4. Heat map for Pearson's correlation coefficients of soil aggregates and soil chemical properties mixed broad-leaved Korean pine forest (BKPF) (**A**) and artificial Korean pine forest (KPP) (**B**) in Northeast (NE) China. The chemical properties were identified in each sample by circle size and colors deduced from −1.0 to +1.0. Abbreviations: hydrogen ions (H^+); potassium ions (K^+); magnesium ions (Mg^{2+}); manganese ions (Mn^{2+}); sodium ions (Na^+); calcium ions (Ca^{2+}); aluminum ions (Al^{3+}); iron ions (Fe^{3+}); effective cation exchange capacity (ECEC); base saturation percentage (BS%); effective acidity (EA); ammonium ($NH_4{}^+$-N); nitrate ($NO_3{}^+$-N); total nitrogen (TN); soil organic carbon (SOC); soil pH.

4.4. Interrelation of Soil Properties with the Soil Related Environmental Parameters

The redundancy analysis (RDA) revealed the interrelations between soil properties and soil related environmental parameters (soil pH, EA, BS%, ECEC, H^+, Fe^{3+}, and Al^{3+}) (Figure 5). The first and second axis of RDA accounted for 47.2% and 15.3% of the total variations, respectively. Al^{3+}, H^+, and ECEC have a strong positive effect on TP, NO_3, AP K^+, Ca^{2+}, and NH_4–N, with a strong negative effect on the proportion % and TN (Figure 5). Similarly, E.A has a strong positive impact on SOC, Mn^{2+}, and proportion %, with a weak correlation with AP, TP, NO_3–N, Ca^{2+}, and K^+. However, Fe^{3+}, BS, and pH weakly correlated to either parameter (Figure 5).

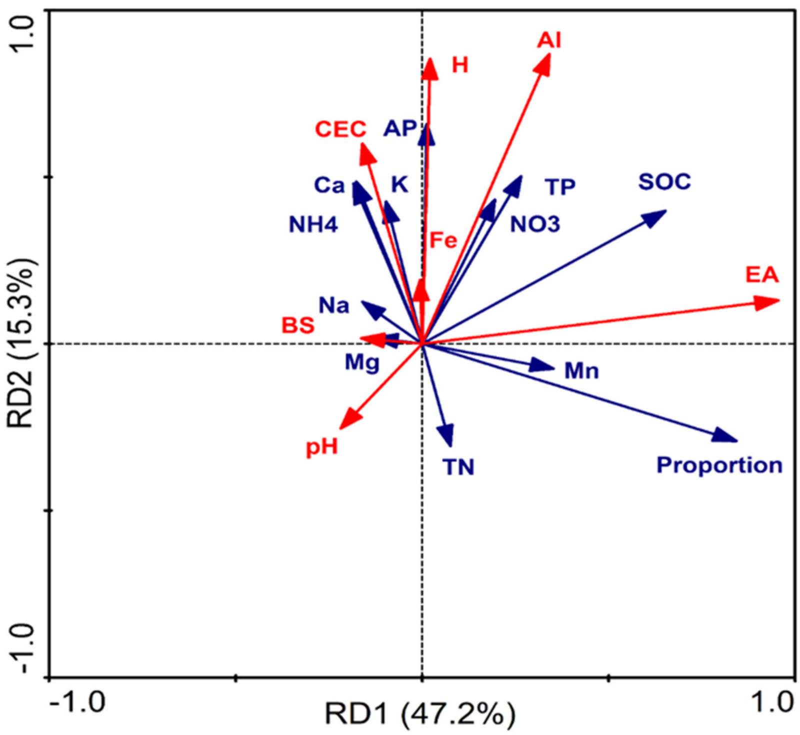

Figure 5. The redundancy analysis (RDA) for soil properties from 0–20 cm soil depths in three replications at mixed broad-leaved Korean pine forest (BKPF) and artificial Korean pine forest (KPP), at four combined (NP) levels of fertilization (CK, 0 g N, and P), i.e., low (5 g N m^{-2} a^{-1}; 5 g P m^{-2} a^{-1}), medium (15 g N m^{-2} a^{-1} + 10 g P m^{-2} a^{-1}), and high fertilization (30 g N m^{-2} a^{-1}; 20 g P g m^{-2} a^{-1}). Hydrogen ions (H); potassium ions (K); magnesium ions (Mg); manganese ions (Mn); sodium ions (Na); calcium ions (Ca); aluminum ions (Al); iron ions (Fe); effective cation exchange capacity (ECEC); base saturation percentage (BS); effective acidity (EA); ammonium ($NH_4{}^+$-N); nitrate ($NO_3{}^-$-N); total nitrogen (TN); soil organic carbon (SOC); and total phosphorus (TP).

5. Discussion

The results of this study showed that pH significantly decreased in medium and high doses of NP, across all the soil aggregates in (BKPF) broadleaf Korean pine and (KPP) artificial Korean pine forests. In our results, the soil PH was generally observed in the range of 5.4–5.72 for BKPF, while it varied between 5.54–5.76 initially; however, the addition of NP significantly decreased the value, especially under high fertilization rates. The same was stated by Mao et al. [43], who revealed that NP addition significantly decreased soil pH, and a significant increase was observed in soil exchange Al/Ca ratio; however, they also studied the impact of N and P as a single treatment, as well as in the form of combination, and the phosphorus-treated plot does not implicate significant effects on the soil PH and Al/Ca ratio. The cause of the increase in effective acidity (E.A) across large macro-aggregates remains stable in meso and micro-aggregates. These findings are in line with the previous study of Zarif et al. [44], wherein they reported that the addition of fertilizer causes acidification, decreases pH, and increases effective acidity—a significant increase in E.A in medium and high NP additional plots showed an increase of nitrification process and Al and Fe's solubilization was responsible for decreasing P binding considerably [12,45].

Our results are in line with the previous study of Wang et al. [39], who reported that BS% and pH decreased significantly by N addition in two different temperate forests [46,47]. This proves that the addition of P causes a buffering effect and keeps pH stable [12,43,44]. The cation pool's composition trend also shows that the targeted forests are probably approaching Al buffering stage. This indicates that the significant increase in Al/Ca ratios and decrease in BS% may cause the trees at a high risk of Al stress [13,43,46]. These results also confirm the previous study conducted in mono and mixed plantations in the temperate zone of northeast China, where a significant increase in Al/Ca ratio was observed in N additional plots [44]. In addition to that, a similar kind of pattern was also observed after long-term fertilization addition in tropical forests, where it was proposed that N saturation was a major cause of N-induced soil acidification [43]. This may attribute to the base cation depletion within soil aggregates, which accelerate a reduction in the buffering capacity of the soil and increase soil acidification [38]. However, Mori et al. [47] found that exchangeable cations and base saturation percentages remain stable under P addition. In another study, it was revealed that an increase in exchangeable base cations, in a two-year of P fertilization experiment, increased Fe^{3+} and Al^{3+} ions, which could be responsible for the decline in base cations, such as Ca^{2+} and Mg^{2+}. Which may be responsible for nutrient degradation and acidification, all of which have a negative impact on forest health and fertility [11,48].

Interestingly, we observed no significant effect of fertilization on Na^+ and K^+ concentration. This might be because of the selective weathering and depletion of particular base cations, such as Ca^{2+} and Mg^{2+} [49]. Our study is in line with Lu et al. [50], who reported that selective weathering of base cations, such as Ca > Na > Mg > K, causes a decrease in base cation budgets and the imbalance of metal ions in the soil. Studies also suggest that the source of nitrogen fertilization may also affect the displacement of the cations. For example, Lucas et al. [51] stated that the use of NH_4NO_3 decreased Ca^{2+}, Mg^{2+}, and K from bulk soils, while the use of ammonium sulphate [$(NH_4)_2SO_4$] decreased Ca^{2+} ions. In our study, the nitrogen source was also ammonium sulphate; however, an increase in both Ca^{2+} and Mg^{2+} was observed. Such differences from fertilizer sources needs to be cleared up in the future studies. Previously, Katou et al. [52] stated the influence of NH_4–N to displace base cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+). They further stated that base cations are displaced and bind to the soil surface, which is easily leached down, thus reducing the buffering against acidification [53]. Our study observed a significant increase of NO_3–N, with high NP application within large macro-aggregates across BKPF and KPP. At the same time, NH_4 remains stable with NP fertilizer application. The non-significant effect of NH_4–N indicates an increase in nitrification and decrease in ammonification, suggesting that the forest is going toward the saturation of N [54]. N inputs can create a balance between the production and consumption of the H^+ ion and play a significant role in N mineralization. Furthermore, Al^{3+} is hydrolyzed and H^+ is released into the soil solution, lowering the pH [55]; our findings support the argument, demonstrating that exchangeable acid cations (H^+ and Al^{+3}), predominated in soil cation pools, with both amounts considerably higher than any base cation at the equivalent base. These cation composition trends often indicate that the forest soils are heading to the Al buffering stage [13].

Our study observed a significant decrease in Ca^{2+} and Mg^{2+} in medium and high NP additional plots across all aggregates and forests. Previously, many scientists have stated that N fertilization over scale can alter the base cation pool size, both in terrestrial and aquatic ecosystems [56–59]. Mao et al. [43] also claimed a decrease in soil exchangeable Ca^{2+}, but other cations remained unaffected. The result obtained in our study stated increase in Ca^{2+} and mg ions while other cations (Mn^{2+}, Na^+, and K^+ remained constant). Our results are in accordance with the previous study, conducted by Lu et al. [60]; they reported an increase in Al^{3+} and H^+, with a decrease in Ca^{2+} and Mg^{2+}, in three contrasting tropical forests forest. High concentrations of Al oxides and low BS have also been found in many other tropical ecosystems. In addition to that, we also observed that there was no significant effect of fertilization on soil total P, which attributes that there is a balance between net litter input and net nutrients output of the plant uptake. Carbon rise may be attributed to lower litter decomposition under medium- and high-nitrogen additives, as well as N inhibition of lignin-degrading microbial enzymes [54,61,62]. This also indicates that the addition results in a surplus of surface nitrogen and reduction in litter decomposer demand for nitrogen [54,61]. Generally, soil C concentration processes under N additions are influenced by the original N concentration in the soil, plant types, forest form, and site conditions [63]. Interestingly, we observed no significant impact of low dose fertilization on soil acidity across the two forest types in all soil aggregates. Our results revealed that soil conditions, among the two studied forests, were significantly affected by the applied fertilizers. The response of N and P towards soil conditions is based on many factors. Among them, site conditions and environmental factors influence the acidification resultant of N application. A high amount of organic matter in soil can suppress acidification because a greater cation exchange capacity is present, as compared to mineral soils [64,65]. Our results are similar to that of Gundersen et al. [66] they stated that soils with N saturation are likely to be more prone to soil acidification. Tree species also play an important role in the determination of factors contributing in soil acidification, generally conifer tree species acidify soils more, as compared to non-conifers type species [67,68]. Conifers tend to secrete organic acids by mycorrhizal rots and absorb base cations [69]. All such biotic and abiotic factors are indicators of the N response to acidification in various ecosystems. Hence, we can say that only addition of NP in soil does not determine the level of acidification caused through them; however, the studies related to interaction between environmental factors, soil microorganisms, and their mode of action need to be studied in detail. The initial/control soil plots are actual representatives of soil environment that influence the end results of the experiment.

6. Conclusions

Our study revealed that, with medium and high doses of combined N and P fertilizer pH, Ca^{2+} Mg^{2+} BS% decreased within large macro-aggregate sizes across forests. Similarly, E.A, Al:Ca, exchangeable Al^{3+}, Fe^{3+}, and H^{+} increased with medium and high doses of fertilizer. This suggests that the addition of nitrogen reduces Ca^{2+} and Mg^{2+}, and the depletion of Ca^{2+} and Mg^{2+} causes an increase in Al^{3+} and H^{+} inside large-macro aggregates, which causes soil acidification, which eventually has an effect on forest fertility and health. Overall, the concentration of base cations is ranked as BKPF > KPP. A significant increase in the Al/Ca ratio indicates that forests are under Al stress and approaching Al buffering. The addition of P had a buffering impact, but it did not help to reduce soil acidity. Nutrient imbalances will result from changes in the availability elements among soil fractions, which are responsible for different nutrient retention and cycling processes. This research provided in-depth knowledge of the factors that will influence soil acidification in a temperate ecosystem.

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