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Impact of Simulated Acid Rain on Soil Base Cations Dissolution between *Eucalyptus* Pure Plantations and *Eucalyptus–Castanopsis fissa* Mixed Plantations

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Abstract: The soils of *Eucalyptus* pure plantations and *Eucalyptus–Castanopsis fissa* mixed plantations were studied using soil column leaching experiments with acid solutions to mimic the effects of acid rain on the soils. This helped researchers learn more about how soil base ions react to acid deposition and their ability to protect the soil from excessive acidity under pure and mixed-species plantations. The results showed that acid rain leaching increased the leaching loss, desorption, and desorption rate of soil base ions while decreasing the soil pH value, adsorption, and adsorption rate of soil base ions. The soil pH value and the leaching loss ranges of K^+, Na^+, and Mg^{2+} were all greater in the pure plantations than in the mixed plantations, while the leaching range of Ca^{2+} was greater in the mixed plantation than in the pure plantations. In the two types of plantations, the adsorption rates of Ca^{2+} and Na^+ in the mixed plantations were higher than in the pure plantations, while K^+ and Mg^{2+} showed higher adsorption rates in the pure plantations than in the mixed plantations. Therefore, soil pH and base ions were greatly affected by the pH value of acid rain. Compared with the pure plantations, the establishment of *Eucalyptus–Castanopsis fissa* mixed plantations can slow soil acidification and leaching of K^+, Na^+, and Mg^{2+} and contribute to the adsorption of Ca^{2+} and Na^+, which is beneficial for the soil nutrient fixation of *Eucalyptus* plantations. The mixed plantations were found to increase the exchange reaction between H^+ and base ions, thereby improving the acid buffer performance of the soil. This, in turn, helped to mitigate the decline in soil fertility. Therefore, establishment of *Eucalyptus–Castanopsis fissa* mixed-species plantations can slow down the impact of acid rain on soil acidification in artificial plantation land to a certain extent and play an important role in optimizing the plantation structure of *Eucalyptus* stands and maintaining their productivity.

Keywords: *Eucalyptus* plantations; acid deposition; base cations; adsorption; desorption

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1. Introduction

Two concerns facing the environment on a worldwide scale are acid rain and the acidity of soil. China now has the third-highest amount of acid rain in the world after Europe and North America [1]. Approximately 5.0 percent of China's land area is currently affected by acid rain, mainly distributed in the area south of the Yangtze River and east of the Yunnan-Guizhou Plateau [2]. Numerous studies have demonstrated that the intensification of soil acidification in acid rain areas, particularly in regions with high temperatures and rainy climates, leads to the leaching of nutrient ions, increasing soil impoverishment, inevitably degrading forest soil and decreasing forest productivity, and polluting surface and groundwater, thereby becoming the principal factors impeding soil fertility and environmental quality [3,4]. In recent years, therefore, there has been a rise in awareness of the effects of acid rain on terrestrial ecosystems.

Forest soil is an important part of the terrestrial ecosystem by serving the nutrients needed for plant growth [5,6]. Soil cations (K^+, Na^+, Ca^{2+}, and Mg^{2+}) are necessary nutrients for plants and may be easily leached by exchanging with H^+, leading to the decreased ability of soil to neutralize acid and the depletion of soil nutrient levels, further affecting the normal physiological metabolism of plants and reducing the nutrient efficiency of forest growth [7,8]. It is well documented that a decreased number of soil microorganisms, declining soil respiration, and slowing decomposition rate of litter under acid deposition are not conducive to the circulation of soil nutrients [9–12]. Changes in soil pH, the release of base ions, and weathering of minerals all directly or indirectly reflect the process of soil acidification, further causing soil degradation and affecting plant nutrient absorption.

Eucalyptus is an important commercial tree species grown in tropical and subtropical areas with a high demand for wood with multiple uses. For the timber and textile industries, *Eucalyptus* plantations have the potential to be a valuable resource. However, to achieve high productivity and increase economic income, forest management, such as the continuous planting of pure plantations [13], application of chemical fertilizers, and short rotation management, were widely applied to *Eucalyptus* plantations in most countries (including China). This caused soil acidification, fertility decline, and decreased woodland productivity, threatening the sustainability of soil fertility [14]. It was found that the soil pH value of *Eucalyptus* plantations showed an upward trend with increased plant age [15], and controlled burning and clearing caused severe losses of soil nutrients in forest soil [16,17].

Eucalyptus plantations are primarily planted in areas with a high prevalence of acid rain and aluminized acidic soil, as found in southern China [1]. Although *Eucalyptus* has a good ability to resist acid rain stress, acid rain still significantly inhibits its growth and nutrient absorption. In [18,19], the authors studied the changes in soil pH and the migration of base cations of the main acid soil types under the influence of simulated acid rain in southern China. They found that acid rain led to the leaching of soil base cations. As the pH value of the acid rain solution decreased, soil acidification intensified, and the leaching of base cations increased. One of the most fundamental physical and chemical processes of ions is adsorption-desorption, which has a significant impact on ion concentration, bioavailability, movement, and transformation in the environment. It would be worthwhile to further investigate the impact of acid deposition on soil base ions in *Eucalyptus* plantations.

In order to address the adverse impacts of acid deposition and soil acidification, measures can be taken to reduce the emission of acid-forming pollutants and to enhance soil management practices, such as soil amendments or cultivation practices to neutralize soil acidity. In recent years, to improve nutrient absorption and utilization efficacy as well as the pH values of *Eucalyptus* planted soil, mixed cultivation of *Eucalyptus* with other tree species has been initiated [20]. This approach aims to increase and sustain the quality of forest land while improving nutrient levels. *Castanopsis fissa* is an evergreen tree of the Fagaceae family and is one of the pioneer species in secondary forests. This broad-leaf tree is characterized by wide adaptability, straight trunks, lush foliage, a large amount of litter, and easy decomposition, contributing to effectively improving soil organic matter, nutrient content, soil enzyme activity, soil fertility, and water conservation [21]. These traits make *Castanopsis fissa* suitable as a mixed species with *Eucalyptus* to improve soil fertility.

In this study, the soil column experiment was set up under simulated acid rain treatments. The soils of five-year-old pure *Eucalyptus* plantations and *Eucalyptus–Castanopsis fissa* mixed plantations were used to analyze the amount of base ion (K^+, Na^+, Ca^{2+}, and Mg^{2+}) leaching, adsorption, and desorption and compare the buffering capacity to acid rain, providing a basis for assessing the soil sensitivity to acid deposition in *Eucalyptus* plantations. In the meantime, the role that mixed plantations play in reducing the acidity of plantation soil was highlighted as an important factor in achieving the sustainable use of plantation land.

2. Materials and Methods

2.1. Sampling Site

The sampling site is located in the Guangxi Gaofeng state-owned forest farm in the northern suburb of Nanning (108°08′–108°53′ E, 22°49′–23°15′ N), which has a subtropical monsoon climate, an annual average temperature of 21.8 °C, an annual average rainfall of 1350 mm, and an average relative humidity of 79%. The soil consists of red soil formed by sand shale, which is ideal for water and nutrient retention. The forest samples were collected in June 2021 and consisted of soil from 5-year-old pure *Eucalyptus* plantations and *Eucalyptus–Castanopsis fissa* mixed plantations (mixed ratio 1:1, planting in alternate rows with a spacing of 2 m × 3 m). The land is below 450 m in elevation, and both forests were at a relative elevation of 50–100 m in the middle hills (Table 1). The fertilization, weeding, and other forest-tending methods for each treatment were consistent.

Table 1. Basic information and soil physical and chemical properties of sample plots.

Stand Type	Terrain			Stand Conditions				Soil Physical Properties			
	Stand Age (a)	Slope Aspect	Slope Position	Stand Density ($Trees \cdot ha^{-1}$)	Average DBH /(cm)	Average Height /(m)	Natural Water Content /(%)	Soil Bulk Density /($g \cdot cm^{-3}$)	Maximum Water-Holding Capacity /(%)	Total Porosity /(%)	Soil Aeration /(%)
PE	5 years	South	Middle	1400	28.7	21.6	21.78	1.48	32.75	48.06	16.14
MED	5 years	South	Middle	700/700	30.2/8.45	22.8/7.14	18.65	1.62	26.47	42.75	12.65

Stand Type	Soil Chemical Properties				
	pH Value	Total Nitrogen ($g \cdot kg^{-1}$)	Nitrate Nitrogen ($mg \cdot kg^{-1}$)	Ammoniacal Nitrogen ($mg \cdot kg^{-1}$)	Available Phosphorus ($mg \cdot kg^{-1}$)
PE	5.22	1.02	20.25	22.05	7.4
MED	5.89	1.21	22.03	24.40	9.0

Note: PE, pure *Eucalyptus* plantations; MED, mixed plantations of *Eucalyptus* and *Castanopsis fissa*.

2.2. Sampling Method

In pure *Eucalyptus* plantations and *Eucalyptus–Castanopsis fissa* mixed plantations, there were a total of six plots, each comprised of three sample sets of 20 m × 20 m (400 m^2). A five-point sampling method was utilized to collect soil sample cores, ranging from 0 to 20 cm deep, from each plot. After the invasive elements in the soil, such as plant residues and stones, were extracted, the soil was packaged in plastic bags in order to make it ready for soil column leaching as well as isothermal adsorption and desorption experiments.

2.3. Experimental Design

2.3.1. Experimental Preparation

According to the characteristics of acid rain in Guangxi and the average ion composition ratio in the precipitation [22], H_2SO_4 and HNO_3 (analytical pure reagents) were mixed at a molar ratio of 8:1 to prepare an acid solution and were diluted with deionized water. Three concentrations of simulated acid rain were prepared at pH values of 3.0, 4.0, and 5.6; meanwhile, pure water at a pH value of 6.0 was used as a control (CK). The soil samples that were taken from each plot of the 5-year-old pure *Eucalyptus* plantations and the mixed *Eucalyptus–Castanopsis fissa* plantations were each thoroughly mixed into one composite sample, then divided into two parts. One part was used for the soil column leaching experiment, and the other part was ground to pass through a 0.2 mm sieve to determine the soil properties after being air dried.

2.3.2. Soil Column Leaching Experiment

The mixed soil samples were packed into 4 plastic PVC pipes (40 cm height, 7.5 cm inner diameter) for the 4 separate treatments with acid solutions. The surface of the 20 cm height soil column was paved with 0.5 cm of river sand to facilitate uniform infiltration of the acid solution and reduce the evaporation of soil water. To inhibit microbial activity, 0.25 mL of chloroform was added to each solution. The simulated acid rain solution was poured into an infusion bag (1 L) for leaching. Referring to the annual average precipitation in the main growing area of *Eucalyptus* and the amount of water flowing into the soil after interception [23], the leaching rate was set at 200 mL/d performed between 10–30 June 2021, lasting for 20 days. At the end of the treatment, the soil samples were completely removed from the PVC pipes. After being air-dried, the soil samples were ground and screened through a 0.2 mm sieve to determine the base cation content of the soil samples and for further adsorption and desorption experiments. The contents of exchangeable soil base cations K^+ and Na^+ were determined by flame photometry (Sherwood M410, Sherwood Scientific Ltd., Cambridge, UK), and the contents of Ca^{2+} and Mg^{2+} were determined by atomic absorption spectroscopy (NOV AA350, Analytik, Jena AG, Jena, Germany) at the Analysis and Testing Research Institute of the Agriculture College of Guangxi University. The pH value of the soil was determined by the Magneto-PHBJ-260 portable pH meter (Shanghai Thunder Magnetic, Shanghai, China).

2.3.3. Isothermal Adsorption and Desorption of Base Cations in Soil

A study was conducted wherein 5 g of soil samples from two distinct types of forest were subjected to varying pH levels of acid rain solutions. An isothermal adsorption test was performed in a 250 mL beaker flask. The centrifugal tubes were each filled with 50 mL of a solution containing KCl, NaCl, $CaCl_2$, and $MgCl_2$ at a concentration of 1 mol/L. To suppress the growth of microorganisms, 0.25 mL of chloroform was introduced into each solution. The tubes underwent agitation for a duration of 24 h at a temperature of 25 °C followed by centrifugation at a speed of 4500 revolutions per minute for a duration of 15 min subsequent to a 2-h period of stillness. In order to analyze the adsorption capacity of the soils, the concentrations of base ions (K^+, Na^+, Ca^{2+}, and Mg^{2+}) were determined using a 10 mL supernatant. After the isothermal adsorption experiment was completed, the remaining suspension was poured out. Then, 10 mL of deionized water was added to the test tube, shaken for 24 h at 25 °C, and centrifuged for 15 min. The concentrations of base ions in the 8 mL supernatant of each tube were determined for further calculation of the base ion desorption amount in the soil.

2.4. Data Analysis

Data were analyzed using IBM SPSS Statistics 21.0 software. Differences in soil pH and base cations (K^+, Na^+, Ca^{2+}, and Mg^{2+}) were tested by ANOVA one-factor deviation. Multiple comparisons of means were performed with the LSD test. A difference in the probability of ANOVA above 95% was considered significant. The formulas for calculating adsorption capacity, desorption capacity, and desorption rate are as follows:

$$Cs = x/m = \frac{(Co - Ce) \cdot V}{M} \tag{1}$$

$$Cs^* = \frac{Ce^* \cdot V}{M} \tag{2}$$

$$Rs = \frac{Cs}{C} \cdot 100\% \tag{3}$$

$$Rd = \frac{Cs^*}{Cs} \cdot 100\% \tag{4}$$

where Cs is the adsorption capacity of base ions (mg·kg^{-1}), Cs^* is the desorption capacity of base ions, Rs is the adsorption rate of base ions, Rd is the desorption rate of base ions, Co is the amount of base ions added during equilibrium adsorption (mg·kg^{-1}), Ce is the amount of base ions in the solution after adsorption equilibrium (mg·L^{-1}), V is the volume of the solution (mL), M is the quality of the soil sample (g), and Ce^* is the concentration of base ions in the solution after desorption equilibrium (mg·L^{-1}).

3. Results

3.1. Effects of Simulated Acid Deposition on the Changes in Soil pH Value in Pure and Mixed Eucalyptus Plantations

The soil acidity in the *Eucalyptus* plantations caused the pH value of the soil to decrease, and soils in both pure *Eucalyptus* and *Eucalyptus* and *Castanopsis fissa* mixed-species plantations reached their minimum pH values after being treated with pH 3.0 (Figure 1). The application of the acid solution had a substantially greater impact on the soil of the pure *Eucalyptus* plantations, and the pH value of the pure *Eucalyptus* plantations' soil was consistently lower than that of the mixed plantings ($p < 0.05$). The soil pH value of pure plantations and mixed-species plantations at the pH 3.0 treatment was reduced by 30.8% and 15.6%, respectively, when compared with the control treatment with a pH of 6.0.

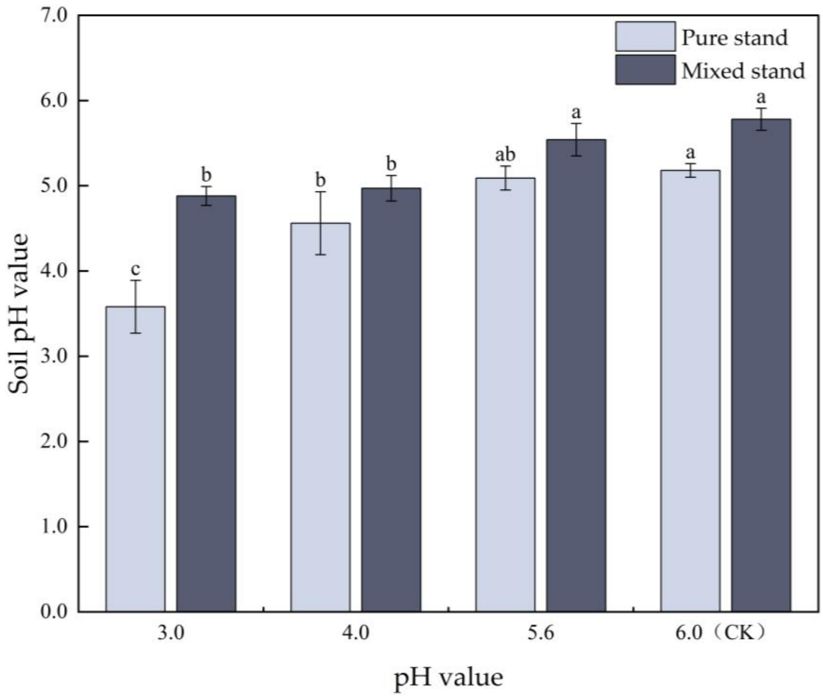

Figure 1. Soil pH value under simulated acid deposition treatments; different letters indicate significant differences at the $p < 0.05$ probability level.

3.2. Effects of Simulated Acid Deposition on the Content of Soil Base Cations in Pure and Mixed Eucalyptus Plantations

The acid solution significantly increased the leaching of base cations from the soil. The leaching loss of base cations in the pure plantations was higher than in the mixed-species plantations at all pH treatments, and the leaching of base ions increased with the decrease in acidity. The amount of base cations leached reached its maximum at a pH of 3.0; more specifically, the amount of Ca^{2+} leached in the pure plantations reached up to 59.17 $mg \cdot kg^{-1}$ at its highest value, whereas the amount of Mg^{2+} leached was minimal (1.8 $mg \cdot kg^{-1}$) among all base cations. In terms of the degree of change that occurred with the pH 3.0 treatment, in comparison to pH 6.0, the quantity of K^+, Na^+, Ca^{2+}, and Mg^{2+} leaching increased by 235.6%, 222.6%, 57.3%, and 306.5%, respectively, in the pure plantation soil. This indicated that in the pure plantation soil, Ca^{2+} has the least significant change of all the cations (Figure 2).

3.3. Effects of Simulated Acid Deposition on Isothermal Adsorption of Soil Base Cations in Pure and Mixed Eucalyptus Plantations

The adsorption ability of soil base ions exhibited an upward trend as the pH value of the acid solution increased (Figure 3). The highest adsorption capacity was recorded at pH 6.0. Moreover, the adsorption percentage of K^+ and Mg^{2+} in the pure plantations was higher than in the mixed plantations; however, the disparity between the two types of plantations decreased with a rise in pH value from pH 3.0 to pH 6.0. The adsorption capacities of K^+ and Mg^{2+} in the soil of the pure and mixed-species plantations exhibited a reduction, with K^+ decreasing from 66.4% to 24.0% and Mg^{2+} from 45.9% to 0.1%. The adsorption capacity of Ca^{2+} and Na^+ in the pure plantations was found to be lower than in the mixed-species plantations, and the variation in the adsorption amount of Ca^{2+} between the two plantations was relatively small, ranging from 1.6% to 8.1%. In contrast, the adsorption amount of Na^+ in the mixed plantations was consistently higher than in the pure plantations, which was over 33.2%. In the two plantations, the adsorption capacities of the soil base ions were, in descending order, $Ca^{2+} > Mg^{2+} > Na^+ > K^+$.

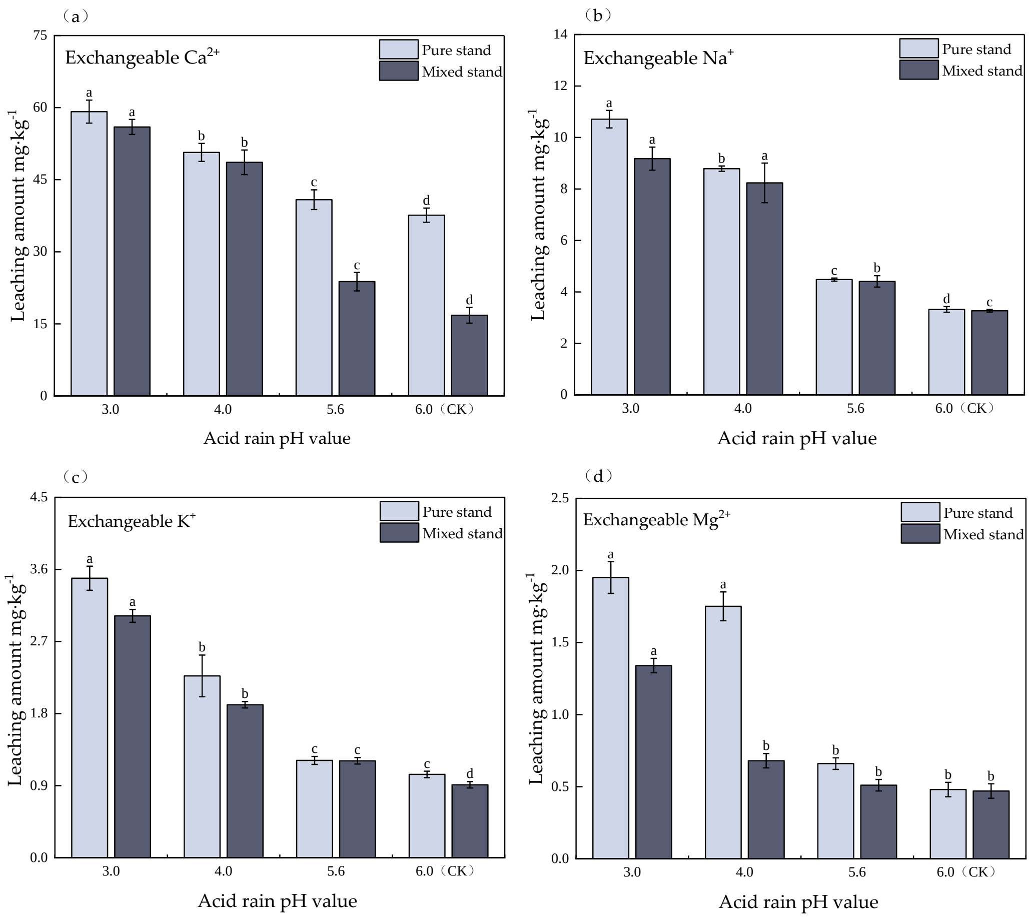

Figure 2. The amount of base cations leached from the soil. Leaching amount of Ca^{2+} (**a**), Leaching amount of Na^+ (**b**), Leaching amount of K^+ (**c**), Leaching amount of Mg^{2+} (**d**). Different letters indicate significant differences at the $p < 0.05$ probability level.

3.4. Effects of Simulated Acid Deposition on Adsorption Rate of Soil Base Cations in Pure and Mixed Eucalyptus Plantations

The adsorption rate of soil base ions was consistent with the adsorption capacity (Figure 4). The results revealed that the adsorption rates of Ca^{2+} and Na^+ in the mixed-species plantations were 1.4%–4.1% and 32.5%–64.3% higher, respectively, than in the pure plantations. Although the adsorption rates of K^+ and Mg^{2+} were higher in the pure plantations than in the mixed plantations due to the increased pH value of the treatment, the adsorption rates of Mg^{2+} in pure plantations and mixed plantations tended to be around 10.8%. Among pure *Eucalyptus* and mixed plantations, Ca^{2+} had the highest adsorption rate for each treatment, exceeding 17.9%, followed by Mg^{2+}, which ranged between 6.2% and 10.0% (Figure 4). The adsorption rate of K^+ ranged from 4.4% to 5%, and Na had the lowest adsorption rate (2.7% to 4.9%) in the pure *Eucalyptus* plantations. Under the pH 3.0 treatment, the adsorption rate of K^+ in the mixed plantations was only 2.7%.

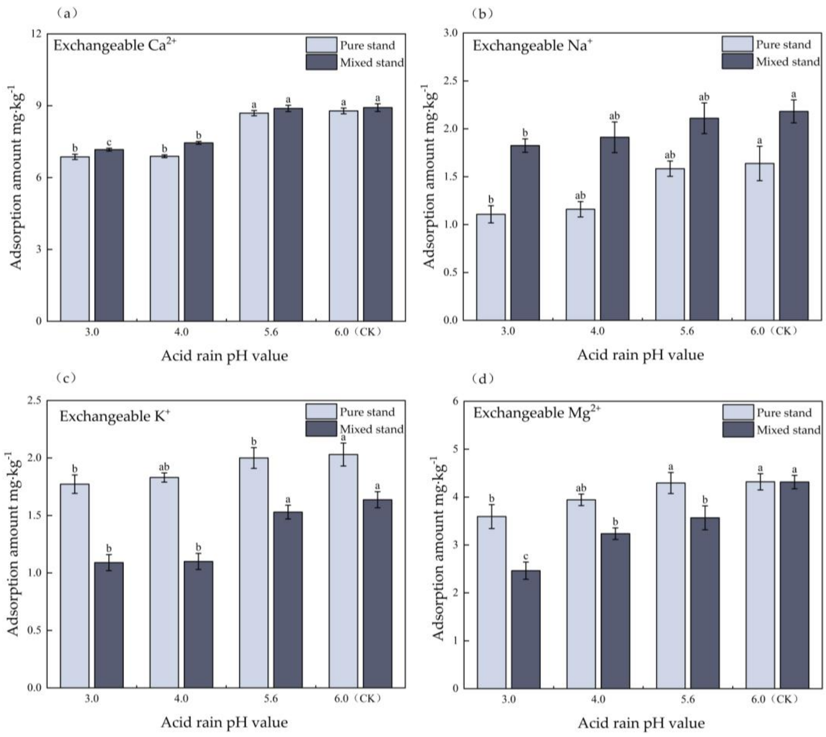

Figure 3. Adsorption amount of soil exchangeable base cations. Adsorption amount of Ca^{2+} (**a**), Adsorption amount of Na^+ (**b**), Adsorption amount of K^+ (**c**), Adsorption amount of Mg^{2+} (**d**). Different letters indicate significant differences at the $p < 0.05$ probability level.

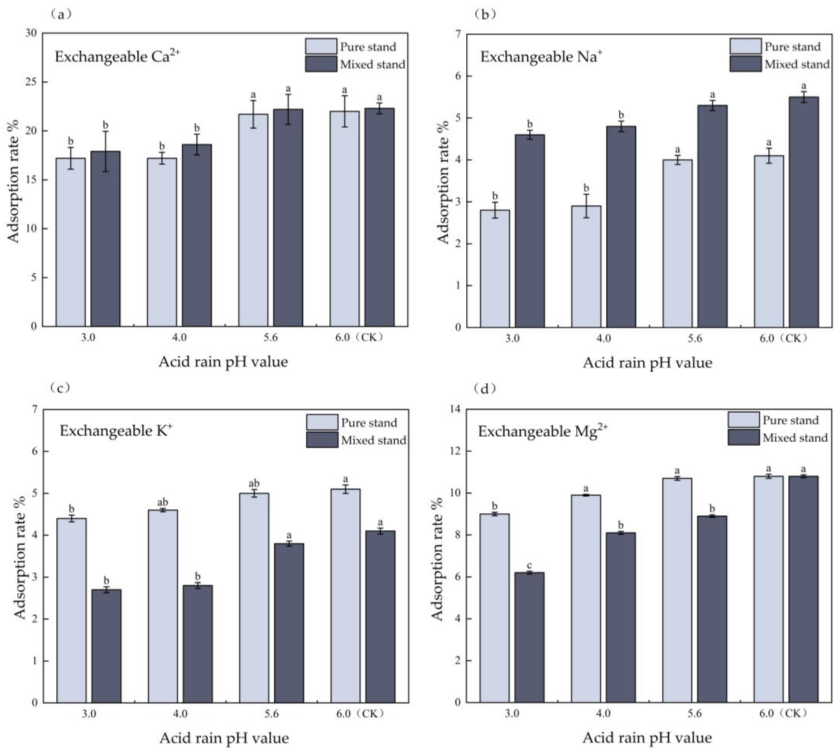

Figure 4. The adsorption rate of soil-exchangeable base cations. Adsorption rate of Ca^{2+} (**a**), Adsorption rate of Na^+ (**b**), Adsorption rate of K^+ (**c**), Adsorption rate of Mg^{2+} (**d**). Different letters indicate significant differences at the $p < 0.05$ probability level.

3.5. Effect of Simulated Acid Deposition on Isothermal Desorption of Base Cations in Pure and Mixed Eucalyptus Plantations

The desorption of soil base ions significantly decreased with the increase in pH value, as illustrated in Figure 5 ($p < 0.05$). The desorption of Ca^{2+} was 7.8%–31.9% lower in the pure plantations compared to the mixed-species plantations. The Na^{+} desorption exhibited significant differences between pure and mixed-species plantations treated with pH 3.0 to pH 6.0, while the largest disparity (31.6% higher in the pure than the mixed-species plantations) was observed at pH 5.6. In other instances, the desorption of Na^{+} in both plantations tended to be equal. The desorption of K^{+} in the soil of pure plantations treated with pH 3.0 was 18.6% higher than in the mixed-species plantations. Conversely, the desorption of K^{+} in the soil of the mixed-species plantations was higher than in the pure plantations for the pH 4.0 to pH 6.0 treatments, resulting in a progressively larger difference ranging from 2.9% to 46.7%. The variations in Mg^{2+} desorption between the two plantations escalated with the acidification of the soil environment, culminating in its maximum value at a pH of 3.0. The desorption rate at this point was found to be 102.1% higher in the pure plantations than the mixed-species plantations.

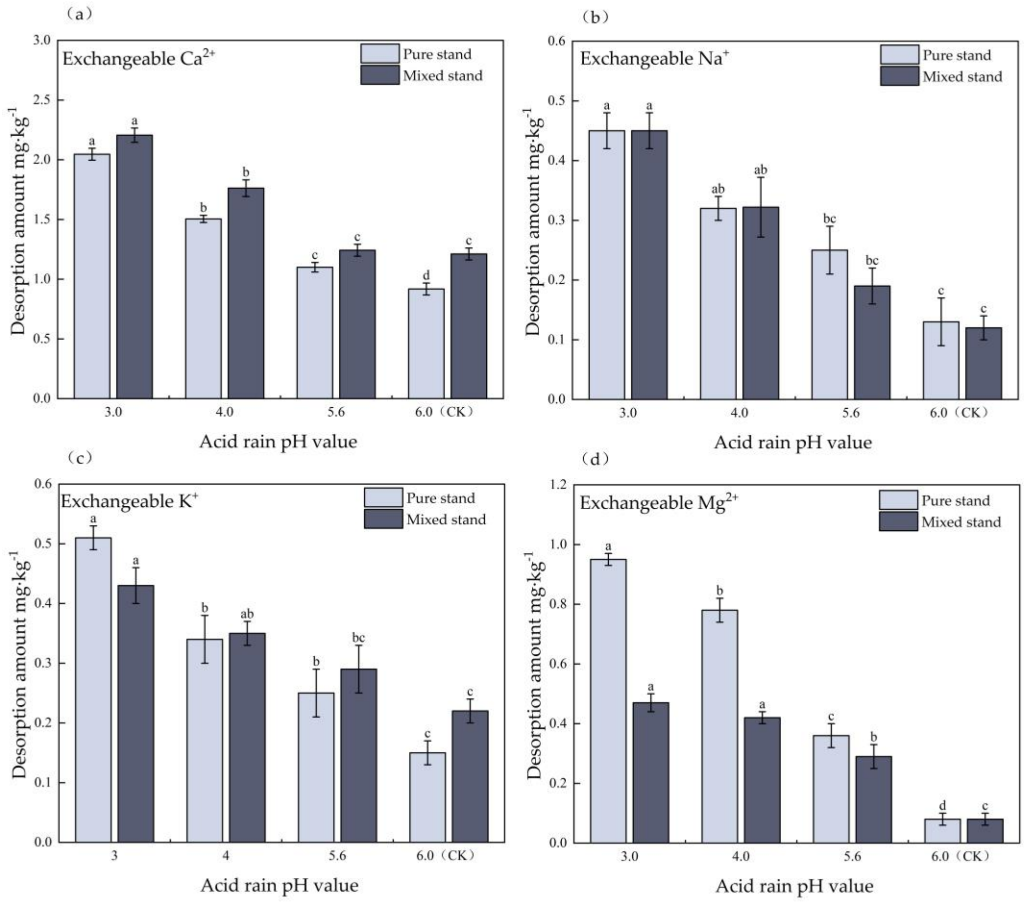

Figure 5. Desorption amount of soil-exchangeable base cations. Desorption amount of Ca^{2+} (**a**), Desorption amount of Na^{+} (**b**), Desorption amount of K^{+} (**c**), Desorption amount of Mg^{2+} (**d**). Different letters indicate significant differences at the $p < 0.05$ probability level.

3.6. Effect of Simulated Acid Deposition on the Average Desorption Rate of Base Cations in the Soil of Eucalyptus Plantations

The desorption rate of base ions increased with increasing acidity. The desorption rates of K^{+}, Na^{+}, Ca^{2+}, and Mg^{2+} in pure plantations fluctuated with the pH value of acid rain, and the highest desorption rate of Ca^{2+} (10.5%) was obtained in the pH 6.0 treatment. From pH 5.6 to pH 3.0, Na^{+} had the highest desorption rate for all treatments, ranging from 15.8% to 40.6%, followed by Ca^{2+}, with desorption rates ranging from 12.7% to 29.8%. Mg^{2+}

had a higher desorption rate than K^+ when treated with pH 4.0, but Mg^{2+} had the lowest desorption rate when treated with other acidity values. In mixed plantations, Ca^{2+} had the highest desorption rate (13.6%) when treated with pH 6.0. From pH 5.6 to pH 3.0, K^+ had the highest base ion desorption rate, followed by Ca^{2+}, Na^+, and Mg^{2+} in order. The Ca^{2+} and K^+ desorption rates in the mixed plantations were 3.4%–29.5% and 36.8%–81.1% higher, respectively, than in the pure plantations. The desorption rates of Na^+ and Mg^{2+} were 43.6%–64.4% and 0%–38.2% higher, respectively, in the pure plantations than in the mixed plantations (Figure 6).

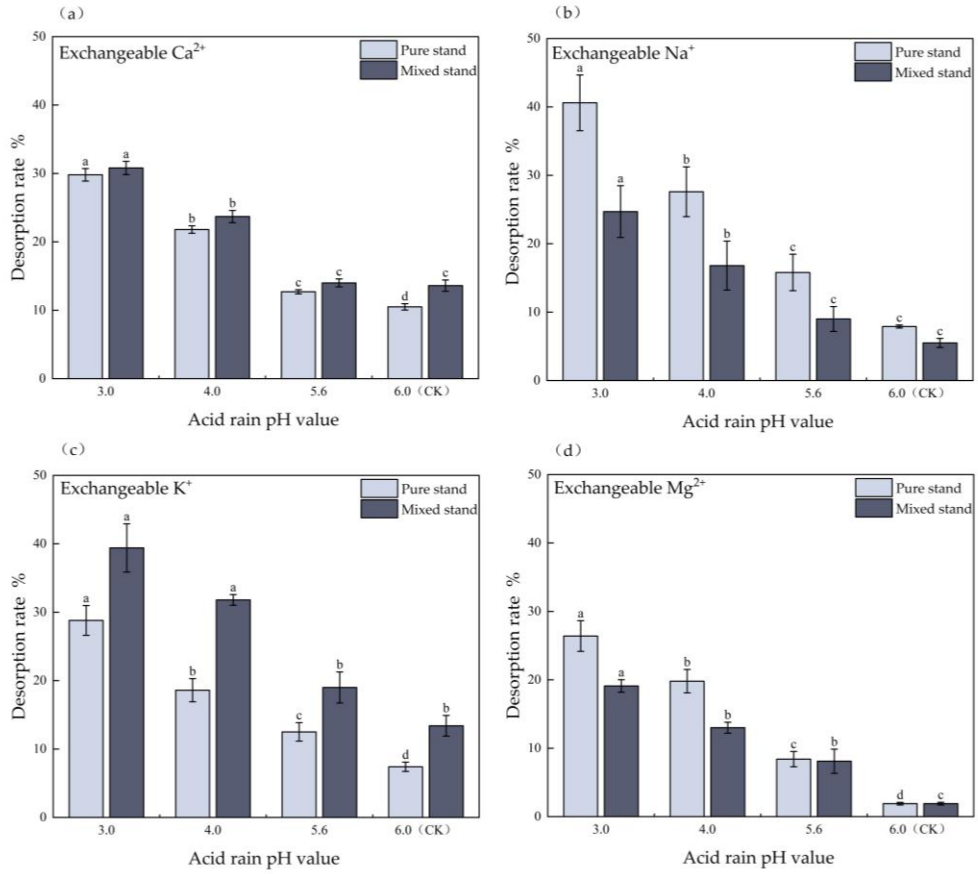

Figure 6. The desorption rate of soil-exchangeable base cations; different letters indicate significant. Desorption rate of Ca^{2+} (**a**), Desorption rate of Na^+ (**b**), Desorption rate of K^+ (**c**), Desorption rate of Mg^{2+} (**d**). Differences at the $p < 0.05$ probability level.

4. Discussion

4.1. Influence of Acid Rain on the Soil Acidity of Eucalyptus and Castanopsis fissa Mixed Plantations

Soil pH value is an important indicator of soil acidification. Under a pH of 6.0, the soil pH value of pure *Eucalyptus* plantations was higher than the mixed plantations. This may be due to the accumulation of *Eucalyptus* root exudates under the plantation leading to an increase in soil acidity. It is also possible that by mixing in broad-leaved tree species like *Castanopsis fissa*, the quantity of forest litter can be increased, which enhances the amount of humus and intermediates in the soil. Additionally, *Castanopsis fissa*, a member of the Fagaceae family, produces litter that includes calcium, which raises the pH of the soil. As a result, the soil retains its favorable qualities for a longer period of time after being cleaned with acidic water [24]. The carboxyl groups in the tree provide a large number of cation exchange sites, neutralize hydrogen ions, and slow down soil acidification. The excess H^+ input into the soil by acid rain results in a lower soil pH and reduced base saturation, leading to soil acidification. Based on the simulated acid rain leaching experiment, it was found that acid rain led to soil acidification with a decrease in soil pH values; the higher the pH value, the less impact acid rain acidification had on the soil [25]. In this study, the pH value of *Eucalyptus* plantations' soil decreased significantly under acid deposition, mainly due to the combination of H^+ and the complex in the soil. This caused a large amount of soluble salt to leach into the soil and the exchangeable base ions on the soil surface. H^+ replaced the cation exchange sites on the soil surface, producing exchangeable acid and aggravating soil acidification.

A pH level of 3.5 is considered a critical point for acid rain as it weakens the soil's buffering capability [26,27]. Soil acidification is observed to increase when the pH level falls below 3.5. However, we found that the acid treatment had a minimal impact on the soil's buffering capability once this threshold was exceeded. We found that the soil pH value decreased at pH 3.0 compared to other pH treatments in the pure *Eucalyptus* plantations, but this phenomenon was not observed in the soil of the mixed plantations. Increased acid rain leaching accelerates soil acidification and decreases soil buffering capability. When the pH value of woodland soil is too low, the fixed Al in the soil is activated under the action of H^+, forming exchangeable Al^{3+} and other active Al. A large amount of active Al absorbed by plants will have a toxic effect on plant roots, inhibiting plant growth [28]. The potential cause could be attributed to the assimilation of anions present in acid precipitation, namely SO_4, NO_3, and CO_3, within the soil ecosystem. It has been shown that the presence of different cations, including calcium, in soil can facilitate the absorption of anions from acid rain [29]. This process leads to the formation of crystalline $CaCO_3$ and $CaCO_4$, which in turn results in an increase in the unconfined compressive strength of the soil. The findings of Gratchev and Towhata [30] suggest that the flux and soak period of acid rain, as well as the buffering capacity and cation exchange capacity (CEC) of soils, are significant factors that may alter the interactions between soil properties and acid rain. From pH 6.0 to pH 3.0, the soil pH value of both plantations decreased to different degrees. The decreased rate of the pure plantations was higher than that of the mixed plantations. Active microorganisms in the soil of mixed plantations may hasten the decomposition of tree litter and improve soil acidification, mainly because there is a certain amount of excessive cations in litter, which helps to neutralize soil acidity [31]. A relevant study found that the decomposition rate of litter in mixed plantations of *Quercus acutissima* and *Robinia pseudoacacia* was higher than in the pure plantations [32]. It is speculated that the decomposition process of ash bark oak litter in this experiment had an ion exchange reaction with soil cations, thus increasing soil organic matter, soil base and underground seepage [33,34]. All these factors contribute to the increase in soil pH value and the decrease in soil total hydrolytic acidity, which helps to further alleviate soil acidification [34]. Therefore, the soil of *Eucalyptus* and *Castanopsis fissa* mixed plantations has a certain buffer capacity for acid deposition, which is conducive to maintaining the normal growth of trees.

4.2. Effect of Soil Salt Ions on Acid Rain Buffering in Pure Eucalyptus Forests and Mixed Forests

Changes in soil pH, the release of base ions, and mineral weathering all directly or indirectly influence the process of soil acidification, and base ions (K^+, Na^+, Ca^{2+}, and Mg^{2+}) in soil are essential nutrients for plants. Nutrients are easily lost by H^+ exchange under acid deposition, leading to a decrease in the soil's ability to neutralize acids and depletion of nutrient banks, which are the main factors hindering the recovery to surface acidification [35,36]. Therefore, the sensitivity of soil to acid deposition is usually associated with the depletion of base ions due to the leaching of ions. Acid deposition accelerates nutrient leaching, and poor soil nutrient output is the main cause of forest degradation [37]. The mechanical characteristics of acid-rain-affected soil may change as a result of changes in the diffuse double layer of the clay size fraction caused by ion exchange and the subsequent changes in the van der Waals forces acting between the clay particles. When soil pH drops, H^+ ions interact with the cations in the clay's diffuse double layer, initiating an exchange process. H^+ ions would likely replace the commonly encountered exchanged cations due to their superior location in the Hofmeister series [30].

Soil acidification is closely related to soil buffering capacity. This important buffering mechanism is achieved by releasing base ions, mainly K^+, Na^+, Ca^{2+}, and Mg^{2+}, which exchange reactions. After the exogenous protons enter the soil, the buffering capacity of the soil is gradually weakened or exhausted with the decrease in soil pH value and large amount of soil exchange cation leaching [38,39]. In particular, Ca^{2+} had the highest leaching amount, which increased gradually with the decrease in the pH value of acid rain [35,40,41]. Studies have shown that soil base ions leached different quantities when the soils were treated with different acidities in three types of subtropical forest in the Dinghushan mountain: evergreen broad-leaved forests, mixed broadleaf–conifer forests, and pure *Pinus massoniana* forests; severe acid deposition resulted in significant decreases in soil base ions, with Ca^{2+} and Mg^{2+} being the most sensitive to acid deposition [42,43]. Our results showed a large amount of leaching of exchangeable K^+, Na^+, Ca^{2+}, and Mg^{2+} in the soil of the *Eucalyptus* plantations because acid deposition causes these base ions to be largely exchanged out of the soil colloidal surface. In the proton buffering process of red soil, Mg^{2+} and Ca^{2+} play a major role. This is especially true of Ca^{2+} because the amount of Ca^{2+} released is much larger than that of Mg^{2+}, and the adsorbed Ca^{2+} in the cation exchange reaction is easy to decompose and release [44]. Under acid deposition leaching, Ca^{2+} can be released from the soil through mineral weathering, thus increasing the amount of Ca^{2+} leached [35]. In pure *Eucalyptus* plantations and *Eucalyptus* and *Castanopsis fissa* mixed plantations, the leaching loss of K^+, Na^+, Ca^{2+}, and Mg^{2+} in the two plantations increased gradually from pH 6.0 to pH 3.0, and the leaching loss of K^+, Mg^{2+}, and Na^+ were greater in the pure forest than in the mixed forest. Among them, Mg^{2+} had the largest leaching range, indicating that Mg^{2+} is sensitive to acid deposition in pure *Eucalyptus* forests. The leaching range of Ca^{2+} in mixed plantations was larger than in pure plantations, indicating that Ca^{2+} plays the most important role in proton buffering in mixed plantations, which contributed to the smaller decrease in the soil pH value of mixed plantations than pure *Eucalyptus* plantations. Furthermore, these cases suggest that Ca^{2+} and Mg^{2+} could be regarded as sensitive indicators of soil acidification in pure *Eucalyptus* plantations and *Eucalyptus* and *Castanopsis fissa* mixed plantations, respectively.

4.3. Characteristics of Adsorption and Desorption of Soil Base Ions in Pure and Mixed Eucalyptus Forests under Acid Deposition

The adsorption capacity and adsorption rate of base ions gradually decreased with the increase in acidity. This was mainly because soil acidification occurred after acid rain leaching, and the H^+ concentration increased, which led to it competing with base cations for exchange sites, resulting in a decrease in the adsorption capacity of base ions. The adsorption capacities of Ca^{2+} and Mg^{2+} were greater than those of K^+ and Na^+, indicating that divalent cations are easier to adsorb. K^+ and Na^+ are mainly adsorbed through electrostatic adsorption, while Ca^{2+} and Mg^{2+} are adsorbed through various methods, such as electrostatic adsorption, hydroxyl complex adsorption, and surface precipitation adsorption, which help to increase their adsorption [45]. In our isotherm adsorption and desorption experiments, the adsorption and desorption amounts and the rate of desorption of Ca^{2+} were the highest among the four cations, which is consistent with the results of a study by [46]. A considerable amount is adsorbed in the soil colloid mainly due to the large Ca^{2+} content in the crust, which was easily decomposed and released during the cation exchange reaction [47]. In addition, the soil releases Ca^{2+} through mineral weathering as shown previously [48]. Ca^{2+} and Mg^{2+} are easily adsorbed by the soil colloid, although Ca^{2+} and Mg^{2+} are sensitive to changes in soil acidity and are prone to leaching under simulated acid deposition [35]. Therefore, considerable amounts of Ca^{2+} and Mg^{2+} were adsorbed in the soil colloid during the isothermal adsorption test, contributing to the large desorption amount after the desorption test. Therefore, the adsorption treatment increased the amount of Ca^{2+} in the soil colloid during the isothermal adsorption test, contributing to the higher rate of desorption following the desorption test. K^+ and Na^+ had the lowest adsorption and desorption amounts after being treated by the simulated acid deposition.

The contents of K^+ and Na^+ were low in the soil due to the weathering of potassium and sodium feldspar. The desorption amounts of K^+ and Na^+ were also related to the clay content of the soil. The higher the clay content, the lower the leaching release of K^+ and Na^+ and the lower the K^+ and Na^+ contents in the soil were [38].

The acid rain led to changes in soil pH value and the release of soil base cations. The test results showed that the desorption amounts and rates of soil base ions increased with the decrease in the pH value of the acid treatment. The main reason was that after the isothermal adsorption test, many base ions were adsorbed in the soil colloid. With the decrease in soil pH value, the increased concentration of H^+ stimulated the exchange reaction with base cations, showing a strong desorption capacity. The desorption amount and rate of base ions increased gradually with the increase in the acidity of the acid solution due to the increase in H^+ concentration, which accelerated the exchange reaction.

When comparing the adsorption and desorption results of soils from pure and mixed-species plantations, it was noted that the adsorption rates of Ca^{2+} and Na^+ in mixed-species plantations were higher than in the pure plantations. This indicates that mixed forest environments are more favorable for the adsorption of Ca^{2+} and Na^+, whereas pure forests are more conducive to the adsorption of Mg^{2+} and K^+. The desorption rates of four base cations (K^+, Na^+, Ca^{2+}, and Mg^{2+}) exhibited greater increases from pH 6.0 to pH 3.0 in the pure plantations compared to the mixed-species plantations. The results suggest that as acidity levels rise, soil texture is compromised, leading to the adsorption of base ions on the soil colloidal surface, which is not conducive to the fixation of soil base ions. Nevertheless, the accelerated decomposition of litter within mixed plantations and the subsequent promotion of biological circulation have been found to have a positive impact on soil texture. Consequently, this can lead to a decrease in the desorption of soil salt ions within mixed-species plantations.

5. Conclusions

Under simulated acid deposition, the soil pH value, adsorption amount, and adsorption rate of *Eucalyptus* plantations declined with decreasing pH values of acid treatment. In contrast, the change in leaching amount, desorption amount, and desorption rate showed an increasing trend. The findings indicate that the *Eucalyptus* and *Castanopsis fissa* mixed forests exhibited lower levels of leaching loss and soil acidification in comparison to the pure *Eucalyptus* forests across all acid treatments. The acid buffering capacity of the soil was improved due to an increase in the exchange reaction between H^+ and base ions, which resulted in a reduction in soil degradation. The pH value and desorption rate of salt ions in the pure forests exhibited a greater decrease than those in the mixed forests as the pH level decreased from 6.0 to 3.0. Mixed plantations exhibit greater affinity toward the adsorption of Ca^{2+} and Na^+ ions in comparison to pure plantations. The mixed plantations were found to increase the exchange reaction between H^+ and base ions, thereby improving the acid buffer performance of the soil. Additionally, considering the varying reactions of soil salt ions to acid rain in pure *Eucalyptus* forests and mixed *Eucalyptus* forests, it could be an effective strategy to preserve soil fertility in plantation forests by tailoring nutrient supplementation and enhancing organic matter content based on the specific plantation type. However, further field trials are required to determine the additional benefits of long-term extensive mixed-species plantations on acid deposition.

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