

Improving pH buffering capacity of an acid soil to regulate nutrient retention and mitigate water pollution using Calciprill and sodium silicate



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ABSTRACT

In the tropics, high rainfalls and hot temperatures cause the formation of highly weathered acid soils with low pH buffering capacity (pHBC). Such soils are prone to nutrient losses via leaching, surface runoff, and volatilization. The poor nutrient retention of the highly weathered soils can cause environmental pollution in water bodies and detrimentally affect aquatic ecosystem. A preliminary study was conducted by mixing an acid soil (Bekenu series, *Typic Paleudults*) with Calciprill (80 %, 90 %, and 100 % Ca saturation) and sodium silicate (90, 105, 120, 135, and 150 kg ha⁻¹) to determine the effects of the amendments on pH and pHBC of Bekenu series. Furthermore, a soil incubation study was carried out to determine the relationship between pH, pHBC, and effective cation exchange capacity (ECEC) after the soil was applied with Calciprill and sodium silicate and incubated for 40, 80, and 120 days. After the soil was harvested, the relationship between pHBC with soil exchangeable ammonium (NH₄⁺), available nitrate (NO₃⁻), and available phosphorus (P) to determine whether the combined use of Calciprill and sodium silicate is able to mitigate N and P losses through surface runoff and leaching to contaminate the surface and underground water bodies. The results from the studies showed that Calciprill and sodium silicate significantly increased soil pH and pHBC of Bekenu series. Notably, in the soil incubation study, the treatments with Calciprill and sodium silicate consistently improved pHBC compared with the soil without these amendments, suggesting that C2S4 (Calciprill at 90 % Ca saturation and sodium silicate at 135 kg ha⁻¹) is the minimum amount of the amendments required to improve the pHBC of Bekenu series. The significant positive correlation between pH, pHBC, and ECEC throughout the soil incubation study indicates that the amendments are capable of improving pHBC of the Bekenu series when the pH and ECEC increase because of their alkalinity in addition to the presence of carbonate and silicate minerals. The significant positive correlations between pHBC with exchangeable NH₄⁺ and available P at 40 and 80 DAI suggest that the Calciprill and sodium silicate can improve NH₄⁺ and P availability for crop uptake. On the contrary, the significant negative correlation between pHBC and available NO₃⁻ at 80 DAI also suggests that the combined use of amendments can significantly reduce the NO₃⁻ contamination in water bodies because of improved pHBC. The most suitable combination for improving soil pH, ECEC, and pHBC is C2S4 (Calciprill at 90 % Ca saturation and sodium silicate at 135 kg ha⁻¹) and it is possible to co-apply Calciprill and sodium silicate to mitigate NO₃⁻ contamination in water bodies. To further validate the findings of this study, greenhouse study is recommended to elucidate the plant-soil interactions.

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1. Introduction

In the tropics, the highly weathered Ultisols and Oxisols are formed through the abundance of kaolinite clay and iron minerals, excessive rainfalls, and warm temperatures throughout the year [32,34,68]. These soils are generally infertile because they are low in pH, low in organic matter, low in nutrient holding capacity, and low in pHBC. This causes poor retention and excessive losses of plant essential nutrients via surface runoff and leaching [73]. The excessive losses of plant essential nutrients caused contamination of the surface and underground water bodies adjacent to the farming areas, after which this phenomenon detrimentally affects aquatic ecosystem, hence causing encroachment of invasive aquatic weeds on water surfaces [27,73]. Soil acidification and water pollution are exacerbated by other natural processes and anthropogenic activities such as decomposition of organic residues [1,19,79], unbalanced use of fertilizers [2,29,54], industrialization [31,74], intensive farming [51,80,88], and acid rain [39].

Soil pHBC is the ability of a soil to resist the drastic changes of pH when the soil is added with small amounts of acid or base [46]. A soil with low pHBC is characterized by rapid pH change when a small amount of acid or base is added and this significantly influences availability of plant essential nutrients such as NH_4^+ , NO_3^- , and P [32,24]. Without regulating soil pHBC using a proper management approach, farmers often resort using high doses of chemical fertilizers to saturate acid soils with plant essential nutrients although this approach is not economical besides causing environmental pollution such as eutrophication [26,49,73]. For example, when soil pH is less than 5 (Very strongly acid), the excessive concentration of H^+ ions out-compete NH_4^+ from being adsorbed on the soil exchangeable sites, after which the free moving NH_4^+ ions are nitrified into NO_3^- ions [47,48]. Thereafter, the NO_3^- ions and some of the NH_4^+ ions are easily leached to further acidify the soil besides contaminating the water resources [21,85,24,69]. Several related studies opined that excessive use of N and P fertilizers in agriculture is a significant contributor to eutrophication [22,28,36,50]. Furthermore, Al-Asif et al. [4] demonstrated that significant increase in the N and P concentrations in the water bodies can adversely affect the biodiversity and abundance of macrobenthic fauna assemblage at the mangrove areas.

To overcome the aforementioned challenges, it is essential to understand the mechanisms on improving soil pHBC to resist rapid pH changes and mitigate the N and P losses through leaching and surface runoff. It is possible to restore the productivity and improve nutrient retention of these highly weathered acid soils through the combining or compounding fertilizers, liming materials, and inorganic and organic amendments [18,40,58]. Zhang et al. [86] opined that soil pHBC is governed by pH, organic matter, calcium carbonate (CaCO_3), and ECEC. Hamidi et al. [25] and Perumal [58] added that nutrient soil retention and losses are affected by soil pH, pHBC, temperature, redox reactions, and floods. In organic farming, studies showed that using organic amendments such as chicken litter biochar and crop straw biochar at optimum rates significantly ameliorate soil acidity and low pHBC because of the carbonate, organic functional groups, hydroxides, and silicates of these materials [13,72,78]. However, the alkalinity and carbonates of biochar are inconsistent in improving soil pHBC because these properties vary significantly with different pyrolysis temperatures and type of biomass used [77,83]. To end this, it is essential to choose the right type of inorganic liming material at the right amount to provide rapid and consistent neutralization improvement soil pHBC in a manner that N and P losses from the highly weathered acidic soils into surface and underground water resources are significantly reduced.

There is a dearth of information on the combined use of Calciprill and sodium silicate on soil pH, ECEC, and pHBC of Bekenu series (*Typic Paleudults*) in addition to regulating the retention of NH_4^+ , NO_3^- and P and preventing the contamination of water bodies. Thus, the research question on the right combination of Calciprill and sodium silicate to

improve pHBC of Bekenu series over time has not been answered. It is therefore hypothesized that combined use of Calciprill and sodium silicate could improve pHBC of Bekenu series over time. This is because the Calciprill has higher CaCO_3 purity (95 %) and neutralizing value (99) compared with the conventional liming materials, whereas sodium silicate is a highly soluble Si-based fertilizer which could improve soil pH [5,66], stabilize soil structure [37], increase soil water holding capacity [65], and improve nutrient retention [15,46,61]. The Calciprill and sodium silicate are capable of increasing soil pH and ECEC because of their CO_3^{2-} and SiO_3^{2-} , which are reputed for neutralizing excessive H^+ ions in addition to increasing number of negatively-charged sites to retain NH_4^+ . Moreover, they are able to precipitate P from being lost through leaching. Therefore, the objectives of these studies were to determine: (i) the effects of Calciprill and sodium silicate on pH and pHBC of Bekenu series; (ii) the relationship between pH, pHBC, and ECEC for elucidating the mechanisms of the amendments on pHBC improvement; and (iii) the relationship between pHBC with soil exchangeable NH_4^+ , available NO_3^- , and available P to control N and P contamination in surface and underground water bodies. It is hoped that the findings in the studies deepen the understanding on the mechanisms of pHBC improvement through combined use of Calciprill and sodium silicate in the highly weathered acid soils to mitigate N and P pollution in surface and underground water bodies.

2. Materials and methods

2.1. Soil sampling, amendment preparation, and physico-chemical analyses

Based on the USDA classification, the soil (Bekenu series, *Typic Paleudults*) was used for the pHBC study because it is an infertile Ultisol which is characterized by low pH, excessive acidity, and low pHBC because of the excessive rainfalls and hot temperatures throughout the year in Malaysia. In addition, this soil is rich in kaolinite clay minerals, ferric oxide, and other mixed sedimentary rocks with weak medium to coarse sub-angular blocky structure; thus, it is consistently friable and has a well-drained profile [53]. Although this soil is commonly used for the cultivation of oil palm, rubber, and black pepper, a few studies reported that it is prone to nutrient leaching because of its low pH ($\text{pH} < 5$) and low CEC [23,47]. The soil sampling was carried out in an uncultivated area at Universiti Putra Malaysia Bintulu Campus, Sarawak, Malaysia with the geographical coordinates of 03°20'N and 113°07'E (Fig. 1). According to Johan et al. [30], this area has a rainfall rate of approximately 3000 mm per annual with a mean air temperature of 27 °C and relative air humidity of 80 % throughout the year. The soil was sampled in a pedon form with the specifications of 1 m length \times 1 m width \times 0.2 m depth using hoe and shovel. Afterwards, the soil sample was air-dried, manually crushed, sieved to pass a 2 mm sieve, and bulked for homogenization prior to initial characterization and pHBC study. The Calciprill and sodium silicate were supplied by Omya

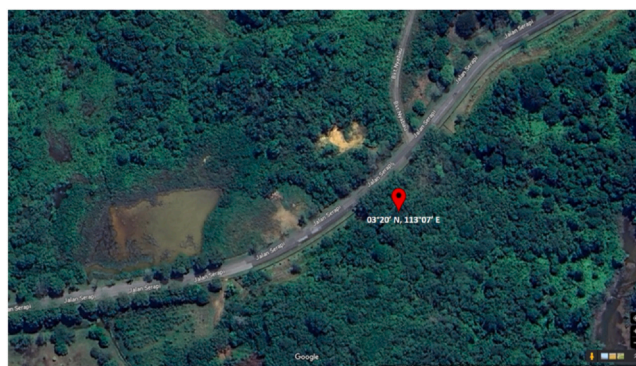


Fig. 1. Aerial view for the location of soil sampling for pH buffering capacity study in Universiti Putra Malaysia Bintulu Sarawak Campus, Malaysia.

Table 1

Selected physico-chemical properties of Bekenu series (*Typic Paleudult*) used in the soil pH buffering capacity study.

Soil physico-chemical properties	Value determined
pH in water	5.13
pH in KCl	3.94
Electrical Conductivity ($\mu\text{S cm}^{-1}$)	8.87
	(mg kg^{-1})
Exchangeable K^+	76.0
Exchangeable Ca^{2+}	17.1
Exchangeable Mg^{2+}	20.4
Exchangeable Na^+	7.8
Exchangeable Fe^{2+}	476.9
Exchangeable Mn^{2+}	6.1
	($\text{cmol}_{(+) } \text{kg}^{-1}$)
Exchangeable acidity	1.21
Exchangeable Al^{3+}	1.03
Exchangeable H^+	0.18
Effective Cation Exchange Capacity	3.45
Crude silica (%)	7.98
pH buffering capacity($\text{mmol H}^+ \text{kg}^{-1} \text{soil pH}^{-1}$)	0.31

Asia Pacific Sdn. Bhd., Kuala Lumpur, Malaysia, and Humibox Sdn. Bhd., Kuala Lumpur, Malaysia, respectively.

The bulked soil sample was analysed for its pH in water, pH in 1 mol dm^{-3} potassium chloride (KCl), and electrical conductivity (EC) using potentiometric method [56], exchangeable cations (K^+ , Ca^{2+} , Mg^{2+} , Na^+ , Fe^{2+} , and Mn^{2+}) using Mehlich-1 double acid method [41], exchangeable acidity and Al^{3+} using acid-base titration method [64], ECEC using summation of charge equivalent of exchangeable cations (K^+ , Ca^{2+} , Mg^{2+} , Na^+ , Fe^{2+} , Mn^{2+} , Al^{3+} , and H^+) [52], crude silica using gravimetric method [82], and pHBC [3], as demonstrated in Table 1. The similar standard procedures were used to determine the selected chemical properties of Calciprill and sodium silicate (pH in water and KCl, EC, exchangeable K^+ , Ca^{2+} , Mg^{2+} , Na^+ , Fe^{2+} , and Mn^{2+} , and ECEC). The elemental composition of Calciprill and sodium silicate was determined using Energy Dispersive X-ray (EDX) (JEOL JSM-IT500 HR). The selected chemical properties and elemental composition of Calciprill and sodium silicate are presented in Tables 2 and 3, respectively.

2.2. Treatment preparation for soil pH buffering capacity analysis (preliminary study)

This pHBC study was conducted in Soil Science Laboratory at the Department of Crop Science in Universiti Putra Malaysia Bintulu Campus, Sarawak, Malaysia. A preliminary study was conducted to determine the effects of Calciprill and sodium silicate addition on pHBC of Bekenu series through the pH and pHBC determination right after the soil was mixed thoroughly with the amendments. A 250 g of sieved soil was weighed using electronic balance for each replicate and kept in a

Table 2

Selected chemical properties of Calciprill and sodium silicate used in the soil pH buffering capacity study.

Chemical properties	Calciprill	Sodium silicate
pH in water	7.77	12.96
pH in KCl	7.78	12.92
Electrical conductivity (dS m^{-1})	3.11	113.17
	($\text{cmol}_{(+) } \text{kg}^{-1}$)	
Exchangeable K^+	0.80	0.67
Exchangeable Ca^{2+}	48.48	trace
Exchangeable Mg^{2+}	0.87	0.02
Exchangeable Na^+	16.55	876.07
Exchangeable Fe^{2+}	0.18	0.11
Exchangeable Mn^{2+}	0.02	0.07
Effective cation exchange capacity	66.90	876.94

Table 3

Elemental composition of Calciprill and sodium silicate using Energy Dispersive X-ray.

Elemental composition	Mass (%)	
	Calciprill	Sodium Silicate
Calcium	25.97 \pm 0.06	8.29 \pm 0.03
Oxygen	57.27 \pm 0.18	57.42 \pm 0.09
Sodium	0.51 \pm 0.03	22.44 \pm 0.07
Silicon	0.62 \pm 0.03	11.85 \pm 0.06
Sulfur	0.79 \pm 0.03	-
Calcium	14.84 \pm 0.15	-
Total	100.00	100.00

plastic container, after which the weighed soil was mixed with the Calciprill and sodium silicate at the pre-determined application rates based on our test crop, black pepper (*Piper nigrum* L.). The application rates of Calciprill were fixed in accordance to the targeted soil Ca saturations at 80 %, 90 %, and 100 % whereby these rates are equivalent to 1.56 g (C1), 1.75 g (C2), and 1.95 g (C3), respectively, per 250 g soil basis [12,42]. For the sodium silicate, the rates were fixed based on the average Si uptake and planting density of black pepper (*Piper nigrum* L.) at 90, 105, 120, 135, and 150 kg ha^{-1} , after which these rates were scaled down to 1.39 g (S1), 1.62 g (S2), 1.85 g (S3), 2.08 g (S4), and 2.31 g (S5), respectively [38,7].

Three rates of Calciprill and five rates of sodium silicate were combined simultaneously and mixed thoroughly with the soil. There was a treatment as soil without any amendment (COS0), which was used to compare the pHBC with the soils with the amendments. There were another two treatments: (i) soils with only Calciprill at 100 % Ca saturation (C3) and (ii) sodium silicate at 150 kg ha^{-1} (S5). These treatments were formulated to determine the separate effect of each amendment on pHBC of Bekenu series. A total of 18 treatments were arranged in a Completely Randomized Design (CRD) with three replications per treatment. Details of the treatments evaluated are summarized in Table 4.

Table 4

Details on treatments evaluated in the soil pH buffering capacity determination (preliminary study).

Code	Treatment		Experimental setup		
	Targeted Ca saturation (%)	Rate per hectare soil (kg ha^{-1})	Rate (g)		
			Soil	Calciprill	Sodium silicate
COS0	0	0	250	0	0
C3	100	0	250	1.95	0
S5	0	150	250	0	2.31
C1S1	80	90	250	1.56	1.39
C1S2	80	105	250	1.56	1.62
C1S3	80	120	250	1.56	1.85
C1S4	80	135	250	1.56	2.08
C1S5	80	150	250	1.56	2.31
C2S1	90	90	250	1.75	1.39
C2S2	90	105	250	1.75	1.62
C2S3	90	120	250	1.75	1.85
C2S4	90	135	250	1.75	2.08
C2S5	90	150	250	1.75	2.31
C3S1	100	90	250	1.95	1.39
C3S2	100	105	250	1.95	1.62
C3S3	100	120	250	1.95	1.85
C3S4	100	135	250	1.95	2.08
C3S5	100	150	250	1.95	2.31

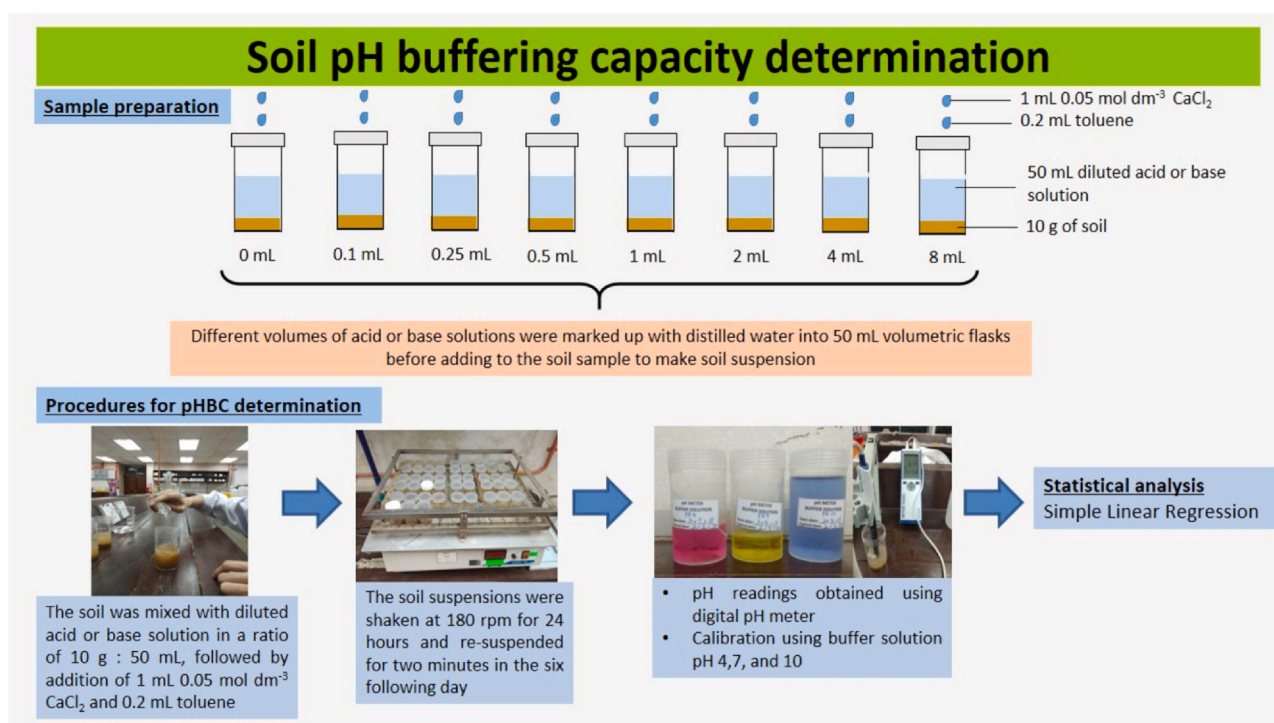


Fig. 2. Details on the procedures of soil buffering capacity determination.

2.3. Soil pH buffering capacity determination

Soil pHBC was determined using the method described by Aitken and Moody [3]. A 10 g of soil was weighed into a 100 mL polyethylene plastic vial and added with 50 mL of 0.1 mol dm⁻³ HCl (if the initial soil pH is more than 5.5) or 0.1 mol dm⁻³ NaOH (if the initial soil pH is less than 5.5) to reduce the suspension effect and to prevent underestimation of acidity in the soil samples [64]. Different volumes (0, 0.1, 0.25, 0.5, 1, 2, 4, and 8 mL) of acid or base solutions were added into 50 mL volumetric flasks after which the acid or base solutions were marked up with distilled water. The soil suspensions were then added with 1 mL of 0.05 mol dm⁻³ CaCl₂ (to reduce variations in ionic strength) and 0.2 mL of toluene (to inhibit microorganism activities). Therefrom, the soil suspensions were shaken at 180 rpm for 24 h using an orbital shaker. The soil suspensions were equilibrated at 180 rpm for two minutes in the following six days to re-suspend the soil solution. After seven days of equilibration, the pH of soil suspension was determined using a digital pH meter (SevenEasy pH, Mettler-Toledo GmbH, Schwerzenbach, Switzerland) with the calibration solutions at pHs 4, 7, and 10. Details on the procedures of soil pHBC study are summarized in Fig. 2. The soil pHBC was computed using the negative reciprocal for the slope of a linear regression to determine the amount of H⁺ or OH⁻ ions added to change the pH by one unit:

Soil pHBC (mmol H⁺ kg⁻¹ soil pH⁻¹) = $-\frac{1}{\text{slope}}$ Where slope is the fitted slope of the regression line.

2.4. Soil incubation study

A soil incubation experiment was conducted in the Soil Science Laboratory at the Department of Crop Science, Universiti Putra Malaysia Bintulu Campus, Sarawak, Malaysia. From the bulked soil, 1 kg of the air-dried soil was weighed using an electronic balance for each replicate and kept in a plastic container with the specifications of 15 cm in diameter and 12 cm in height. Similarly, the application rates of Calciprill and sodium silicate were fixed in accordance with the treatment description outlined in Section 2.3. Based on per one kilogram basis, the application rates of Calciprill were fixed at Ca saturation

of 80 %, 90 %, and 100 % were converted to 6.22, 7.01, and 7.80 g, respectively. The application rates of sodium silicate (90, 105, 120, 135, and 150 kg ha⁻¹) were scaled down to per one kilogram soil basis at 5.55, 6.48, 7.41, 8.33, and 9.26 g, respectively. The treatments for the soils with only Calciprill at 100 % Ca saturation (C3) and sodium silicate at 150 kg ha⁻¹ (S5) were excluded because the objective of this soil incubation study was to determine the effects of combined use of the amendments on pHBC of Bekenu series. Therefore, there were 16 treatments for each batch of the incubation with three replications per treatment which were arranged in a Completely Randomized Design. Details of the treatments evaluated are summarized in Table 5.

Thereafter, the Calciprill, sodium silicate, and soil were mixed

Table 5

Details on treatments evaluated in the soil pH buffering capacity determination (soil incubation study).

Code	Treatment		Experimental setup		
	Targeted Ca saturation (%)	Rate per hectare soil (kg ha ⁻¹)	Rate (g)		
			Soil	Calciprill	Sodium silicate
C0S0	0	0	1000	0	0
C1S1	80	90	1000	6.22	5.55
C1S2	80	105	1000	6.22	6.48
C1S3	80	120	1000	6.22	7.41
C1S4	80	135	1000	6.22	8.33
C1S5	80	150	1000	6.22	9.26
C2S1	90	90	1000	7.01	5.55
C2S2	90	105	1000	7.01	6.48
C2S3	90	120	1000	7.01	7.41
C2S4	90	135	1000	7.01	8.33
C2S5	90	150	1000	7.01	9.26
C3S1	100	90	1000	7.80	5.55
C3S2	100	105	1000	7.80	6.48
C3S3	100	120	1000	7.80	7.41
C3S4	100	135	1000	7.80	8.33
C3S5	100	150	1000	7.80	9.26

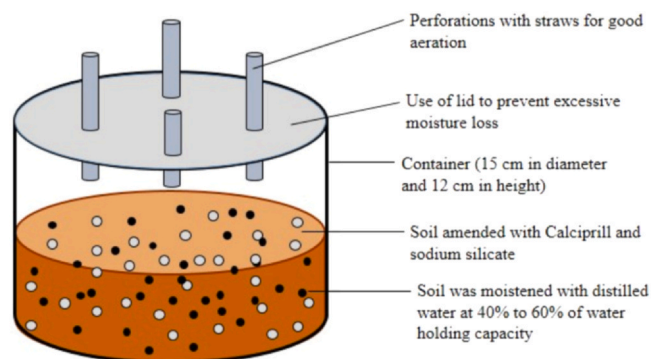


Fig. 3. Set up of experimental unit for soil incubation experiment.

thoroughly. The mixed soil samples were then moistened with distilled in the range of 40% to 60% of the soil water holding capacity and this represented the field capacity of the soil used in this present study. The volume of the distilled water added to each treatment varies because the addition of amendments might have affected the water absorption capacity of Bekenu series. The mixed soil samples were covered with the lid of the container to prevent excessive moisture loss. Each lid had four perforations to enable good aeration. The soil samples were incubated for 40 days, 80 days, and 120 days, respectively. When needed, each soil sample was carefully sprayed with 5 mL of distilled water to maintain sufficient soil moisture for consistent chemical reactions between soil and amendments. At the end of incubation experiment, the soil samples were air dried and manually crushed using mortar and pestle, followed by sieving to pass a 2 mm sieve for pHBC determination using the procedures as described in Section 2.3. The experimental setup for each replication in this soil incubation experiment is demonstrated in Fig. 3.

2.5. Statistical analysis

The collected data were analyzed using Analysis of Variance (ANOVA) to determine the treatment effects using Generalized Linear Model (Proc GLM), thereafter mean comparison was performed using Tukey's Honestly Significant Difference (HSD) test at $p \leq 0.05$. The relationship between amount of H^+ or OH^- added and the change of pH was determined using simple linear regression (Proc Reg) to obtain R-square (R^2) value and regression equation. The correlation analysis was performed using Pearson's correlation (Proc Corr) to examine the relationship between pH, pHBC, and ECEC for elucidating the mechanisms of pHBC improvement through the combined use of Calciprill and sodium silicate. Similarly, the collected data (soil exchangeable NH_4^+ , available NO_3^- , and available P) reported in our previous paper [47] were correlated with pHBC presented in this study to determine the relationship between pHBC with the aforementioned nutrients in mitigating the N and P contamination in the water bodies. The software used was Statistical Analysis System (SAS) version 9.4, Cary, NC, USA.

3. Results and discussion

3.1. Effects of Calciprill and sodium silicate on initial soil pH and pH buffering capacity (preliminary study)

Effects of the Calciprill and sodium silicate on the soil pH are demonstrated in Table 6. The pH values of the soils with Calciprill and sodium silicate significantly increased to a range of 7.56 to 8.05, followed by the soils with sodium silicate only (S5) and Calciprill only (C3) at 7.45 and 7.30, respectively. In contrast, the soil without amendment (COS0) had the lowest pH of 4.27 and this indicates that the Bekenu series is a typical acidic soil which can greatly impair the sorption of NH_4^+ , NO_3^- , and P. This finding further suggests that

Calciprill and sodium silicate were able to mitigate the soil acidity and reduce Al toxicity through neutralization of H^+ . For example, when in contact with soil water, the Calciprill dissolves to release carbonate anions (CO_3^{2-}) which react with active H^+ ions to form carbonic acid (H_2CO_3). In soil water, H_2CO_3 decomposes into carbon dioxide and water molecules [31,30]. Besides, sodium silicate liberates OH^- ions to neutralize active H^+ ions when the orthosilicate anions (SiO_4^{4-}) in the soil solution are transformed into monosilicic acid (H_4SiO_4), thus resulting in increased soil pH [15,17]. Calciprill and sodium silicate are capable of increasing base saturation because of their high inherent contents of base cations such as Ca^{2+} , Na^+ , K^+ , and Mg^{2+} to increase soil pH [11,86,48]. The amendments also impaired Al and Fe hydrolysis, which could significantly exacerbate soil and crop productivity such as stunted crop root growth and P fixation if the soils are not limed [13,60]. This is because when soil pH is higher than 5.5, the presence of OH^- ions in the soil solution will react with exchangeable Al^{3+} and Fe^{3+} ions and transform these acidic cations into insoluble hydroxides through precipitation [44,81].

The significant R^2 values ($R^2 > 0.90$) of the linear relationships indicate that the pHBC of a soil is reflected by the influence of H^+ or OH^- amounts added on the changes of soil pH (Table 6). The soils with the Calciprill and sodium silicate (C1S4, C1S5, C2S2, C2S3, C2S4, C3S3, and C3S4) significantly improved pHBC of Bekenu series compared with the soil without any amendment (COS0) and the soil with sodium silicate only (S5) (Fig. 4). Furthermore, the amendments significantly increased soil pHBC of the afore-stated treatments to a range of 35.4% ($0.42 \text{ mol } H^+ \text{ kg}^{-1} \text{ soil } pH^{-1}$) to 45.2% ($0.45 \text{ mol } H^+ \text{ kg}^{-1} \text{ soil } pH^{-1}$) compared with the untreated soil ($0.31 \text{ mol } H^+ \text{ kg}^{-1} \text{ soil } pH^{-1}$). The high exchangeable acidity and low pHBC of Bekenu series is attributed to its parent material because the kaolinite clay minerals of the soil are formed by red yellow sedimentary rocks which have inherent contents of Al and Fe oxides under high weathering processes caused by high rainfalls and hot temperatures [53]. According to Paramanathan [53], the acidic mineral soil used in this study is characterized by fine loamy texture (18 to 35% clay; more than 15% sand) which resulted in low soil CEC (less than $24 \text{ cmol}_{(+) } \text{ kg}^{-1}$) in a soil depth range of 25 to 100 cm, suggesting that the soil must be amended with Calciprill and sodium silicate to enhance its ability to resist against drastic acidification caused by the addition of acidifying fertilizers and accumulation of carbonic acid through high rainfalls.

On the contrary, the improved pHBC upon the co-application of Calciprill and sodium silicate is related to the increased $CaCO_3$ and ECEC when the soil pH exceeds 7 [75,86,87]. The amendments increased soil pH to an alkaline range of 7.56 to 8.05 from 4.27 (acidic). This increased the concentration of OH^- to neutralize active H^+ in soil solution. When the concentration of H^+ in the soil solution depletes, deprotonation occurs, thus the number of negatively charged exchangeable sites increases on the surface of soil colloids to improve NH_4^+ retention [20]. In this present study, the dissolution of Calciprill and sodium silicate releases CO_3^{2-} and OH^- into the soil solution to neutralize free H^+ ions and this resulted in cation exchange because the exchangeable H^+ were desorbed to maintain its equilibrium in the solution; followed by the adsorption of NH_4^+ on the negatively charged sites in the treated soils [48]. Cai et al. [11] opined that amendments with higher base saturation (K^+ , Ca^{2+} , Mg^{2+} , and Na^+) can immobilize H^+ at the exchangeable sites on soil colloids, which contributed to improved soil pHBC. Moreover, the incomplete dissolution of Calciprill contributed to the enhanced ECEC because the amendment increased the negatively charged surfaces of $CaCO_3$ in the soil for cation exchange to overcome drastic change of soil pH [67,86]. However, Plan [59] reported that the dissolution rate of $CaCO_3$ is influenced by the amount of H^+ ions added and the surface of $CaCO_3$. Continued rainfall and cation removal by crop uptake can accumulate H^+ in soils. Therefore, addition of Calciprill is required to improve pHBC through monitoring soil pH, $CaCO_3$, and ECEC over time.

Table 6

Initial soil pH, regression equations, and the regression coefficient (R^2) to indicate the relationships between the amount of hydrogen or hydroxide ions added and soil pH change in relation to application of Calciprill and sodium silicate.

Treatment	Initial soil pH	Regression equation	R^2
C0S0	4.27 ± 0.02 d	pH = 3.2153 OH ⁻ + 4.704	0.9139*
C3	7.30 ± 0.05 c	pH = - 2.6907 H ⁺ + 7.453	0.9790*
S5	7.45 ± 0.15 bc	pH = - 3.2556 H ⁺ + 7.357	0.9447*
C1S1	7.88 ± 0.14 ab	pH = - 2.5337 H ⁺ + 8.024	0.9433*
C1S2	7.75 ± 0.01 abc	pH = - 2.4789 H ⁺ + 7.817	0.9530*
C1S3	7.61 ± 0.15 abc	pH = - 2.7806 H ⁺ + 7.766	0.9231*
C1S4	7.96 ± 0.07 ab	pH = - 2.3551 H ⁺ + 8.037	0.9136*
C1S5	7.95 ± 0.12 ab	pH = - 2.3445 H ⁺ + 8.011	0.9459*
C2S1	7.56 ± 0.03 abc	pH = - 2.5938 H ⁺ + 7.732	0.9279*
C2S2	7.64 ± 0.04 abc	pH = - 2.3103 H ⁺ + 7.829	0.9115*
C2S3	7.68 ± 0.06 abc	pH = - 2.2382 H ⁺ + 7.912	0.9167*
C2S4	7.76 ± 0.21 abc	pH = - 2.4220 H ⁺ + 7.843	0.9863*
C2S5	8.05 ± 0.11 a	pH = - 2.7742 H ⁺ + 8.105	0.9872*
C3S1	7.72 ± 0.08 ab	pH = - 2.5846 H ⁺ + 7.884	0.9659*
C3S2	8.02 ± 0.05 a	pH = - 2.8091 H ⁺ + 8.015	0.9730*
C3S3	7.84 ± 0.10 ab	pH = - 2.2394 H ⁺ + 8.016	0.9484*
C3S4	7.95 ± 0.03 ab	pH = - 2.3911 H ⁺ + 8.140	0.9787*
C3S5	7.89 ± 0.01 abc	pH = - 2.4443 H ⁺ + 8.086	0.9251*

Note: Different letters indicate significant mean differences using Tukey's HSD test at $p \leq 0.05$. Data are presented as mean ± standard error of three replicates. R^2 values with an asterisk imply the significant relationship at the confidence level of 95 %.

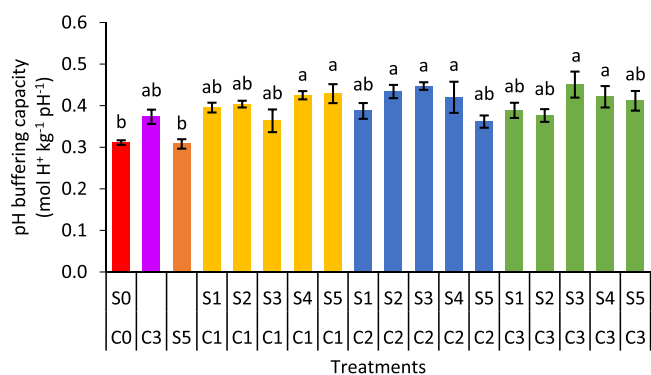


Fig. 4. Soil pH buffering capacity in relation to application of Calciprill and sodium silicate. Different letters indicate significant mean differences using Tukey's HSD test at $p \leq 0.05$. The error bars refer to ± standard error of three replicates.

3.2. Effects of Calciprill and sodium silicate on initial soil pH and pH buffering capacity (soil incubation study)

The combined use of amendments increased the initial soil pH to the alkaline ranges of 7.86 to 8.59 at 40 DAI, 8.13 to 8.53 at 80 DAI, and 8.10 to 8.52 at 120 DAI (Table 7). In contrast, the soil without any amendment was acidic and had the lowest initial pH at 4.29 (40 DAI), 4.13 (80 DAI), and 4.13 (120 DAI). In related studies, Shi et al. [70] and Zhang et al. [86] demonstrated that pH is an important factor which influences the soil pHBC. In this present study, the combined use of Calciprill and sodium silicate treatments was able to increase initial pH of Bekenu series because of the following mechanisms: (i) the release of CO_3^{2-} and SiO_3^{2-} ions to neutralize H^+ ions [31]; (ii) the neutralizing ability of the amendments to mitigate acidity, which resulted in impeded Al and Fe hydrolysis from producing more H^+ [23,44,81,55]; (iii) the release of exchangeable base cations (K^+ , Ca^{2+} , Mg^{2+} , and Na^+) from the amendments can immobilize H^+ at the soil exchangeable sites via cation exchange reaction [11]; (iv) the transformation of orthosilicate ions (SiO_4^{4-}) into monosilicic or polysilicic acids which releases OH^- ions to neutralize H^+ ions in the soil solution [15,86,17].

Based on the regression equations (Table 7), the slope is an important parameter to indicate the pHBC of a soil. The higher slope values suggest that the soil may have a lower ability to resist against the pH changes when the small amounts of acid or base were added because

the slope is inversely proportional to the pHBC. At 40, 80, 120 DAI, it is observed that the soil without any amendment (C0S0) had the slope values of 2.23, 2.60, and 2.53 in the respective regression equations. On the contrary, the slope values for the soils with the co-applied with Calciprill and sodium silicate (C1S1 to C3S5) ranged 0.88 to 2.04, 0.88 to 1.81, and 0.88 to 2.26 at 40, 80, and 120 DAI, respectively. These reduced slope values indicate that the use of amendments improved the pHBC of Bekenu series. At 40, 80, 120 DAI, the significant R^2 values indicate that the pH of Bekenu series changes linearly upon the increasing amount of H^+ and OH^- added. Besides, the significant R^2 values (> 0.85) suggest that the Bekenu series had a low pHBC and it is sensitive to pH changes when small amounts of acid or base were added.

pH buffering capacity refers to the ability of a soil to resist the changes in pH when a small amount of acid or base is added. The higher pHBC of a soil suggests that it has a slower acidification rate at a given amount of exogenous H^+ ions [72]. At 40 and 80 DAI, regardless of the application rate of sodium silicate (S1 to S5), there was no significant improvement in the soil pHBC of the Calciprill at 80 % Ca saturation (C1) compared with that of the soil without any amendment (C0S0). This finding suggests that the Calciprill dominantly improves pHBC of Bekenu series. At 120 DAI, compared with C0S0, the improved pHBC in C1S1 and C1S3 relates dissolution of the Calciprill. Conversely, the pHBC of the soil with Calciprill and sodium silicate (C2S4, C2S5, C3S2, C3S4, and C3S5) was consistently improved to the ranges of 0.81 to 1.12 $\text{mmol H}^+ \text{kg}^{-1} \text{pH}^{-1}$ at 40 DAI and 0.83 to 1.15 $\text{mmol H}^+ \text{kg}^{-1} \text{pH}^{-1}$ at 80 DAI compared with C0S0 at 0.45 $\text{mmol H}^+ \text{kg}^{-1} \text{pH}^{-1}$ (40 DAI) and 0.39 $\text{mmol H}^+ \text{kg}^{-1} \text{pH}^{-1}$ (80 DAI). This finding suggests that C2S4 (7.01 g Calciprill and 8.33 g sodium silicate per one kilogram soil) is the minimum amount of the amendments required to improve the pHBC of Bekenu series. However, at 120 DAI, C3S1 (0.83 $\text{mmol H}^+ \text{kg}^{-1} \text{pH}^{-1}$), C3S4 (0.87 $\text{mmol H}^+ \text{kg}^{-1} \text{pH}^{-1}$), and C3S5 (1.15 $\text{mmol H}^+ \text{kg}^{-1} \text{pH}^{-1}$) had significantly higher pHBC compared with C0S0 (0.40 $\text{mmol H}^+ \text{kg}^{-1} \text{pH}^{-1}$) and notably the pHBC in most of the treatments reduced compared with those at 40 DAI and 80 DAI. This finding indicates that the durability of amendments lasts for less than 120 days and the addition of Calciprill and sodium silicate might be required to maintain the pHBC of Bekenu series over time.

The low pHBC of the soil without any amendment (C0S0) was due to the parent materials and excessive weathering of the Bekenu series. According to Paramananthan [53], Bekenu series is an Ultisol which is typically acidic because it is made up of red yellow sedimentary rocks

Table 7

Initial soil pH, regression equations, and the regression coefficient (R^2) for pH buffering capacity in relation to treatments at forty, eighty, and one hundred and twenty days incubation.

Treatment	Initial pH	Regression equation	R^2
Forty days			
C0S0	4.29 ± 0.05 c	pH = 2.23 OH + 4.67	0.8836*
C1S1	7.86 ± 0.12 b	pH = 1.66 H ⁺ + 8.09	0.9496*
C1S2	8.32 ± 0.04 ab	pH = 1.42 H ⁺ + 8.22	0.9961*
C1S3	8.39 ± 0.04 ab	pH = 1.25 H ⁺ + 8.31	0.9924*
C1S4	8.51 ± 0.07 a	pH = 1.37 H ⁺ + 8.52	0.9828*
C1S5	8.59 ± 0.21 a	pH = 1.71 H ⁺ + 8.66	0.9945*
C2S1	8.10 ± 0.08 ab	pH = 1.67 H ⁺ + 8.16	0.9237*
C2S2	8.21 ± 0.08 ab	pH = 1.80 H ⁺ + 8.29	0.9467*
C2S3	8.45 ± 0.10 a	pH = 2.04 H ⁺ + 8.66	0.8831*
C2S4	8.36 ± 0.12 ab	pH = 1.23 H ⁺ + 8.50	0.9771*
C2S5	8.46 ± 0.12 a	pH = 1.02 H ⁺ + 8.42	0.9621*
C3S1	8.23 ± 0.04 ab	pH = 1.25 H ⁺ + 8.17	0.9040*
C3S2	8.15 ± 0.07 ab	pH = 0.96 H ⁺ + 8.13	0.9597*
C3S3	8.23 ± 0.07 ab	pH = 0.94 H ⁺ + 8.18	0.9349*
C3S4	8.39 ± 0.19 ab	pH = 0.97 H ⁺ + 8.35	0.9122*
C3S5	8.55 ± 0.09 a	pH = 0.88 H ⁺ + 8.51	0.9501*
Eighty days			
C0S0	4.13 ± 0.04 e	pH = 2.60 OH + 4.42	0.8977*
C1S1	8.13 ± 0.07 d	pH = 1.66 H ⁺ + 8.21	0.9673
C1S2	8.38 ± 0.01 abc	pH = 1.77 H ⁺ + 8.49	0.9605
C1S3	8.42 ± 0.02 ab	pH = 1.81 H ⁺ + 8.57	0.9326
C1S4	8.48 ± 0.03 a	pH = 1.73 H ⁺ + 8.64	0.9442
C1S5	8.53 ± 0.05 a	pH = 1.64 H ⁺ + 8.65	0.9417
C2S1	8.23 ± 0.03 bcd	pH = 1.35 H ⁺ + 8.23	0.9680
C2S2	8.37 ± 0.02 abc	pH = 1.43 H ⁺ + 8.41	0.9560
C2S3	8.40 ± 0.03 ab	pH = 1.67 H ⁺ + 8.49	0.9344
C2S4	8.44 ± 0.04 a	pH = 1.22 H ⁺ + 8.54	0.9801
C2S5	8.49 ± 0.05 a	pH = 1.20 H ⁺ + 8.55	0.9602
C3S1	8.18 ± 0.02 cd	pH = 1.31 H ⁺ + 8.23	0.9435
C3S2	8.35 ± 0.02 abc	pH = 1.11 H ⁺ + 8.34	0.9482
C3S3	8.39 ± 0.04 abc	pH = 1.30 H ⁺ + 8.41	0.9313
C3S4	8.44 ± 0.08 a	pH = 1.02 H ⁺ + 8.38	0.9395
C3S5	8.47 ± 0.05 a	pH = 0.88 H ⁺ + 8.50	0.9749
One hundred and twenty days			
C0S0	4.13 ± 0.04 d	pH = 2.53 OH + 4.46	0.8554
C1S1	8.28 ± 0.03 abc	pH = 2.26 H ⁺ + 8.49	0.9320
C1S2	8.26 ± 0.02 abc	pH = 2.24 H ⁺ + 8.48	0.9387
C1S3	8.29 ± 0.04 abc	pH = 2.07 H ⁺ + 8.48	0.9184
C1S4	8.38 ± 0.03 ab	pH = 2.04 H ⁺ + 8.57	0.9132
C1S5	8.45 ± 0.02 a	pH = 1.71 H ⁺ + 8.60	0.9352
C2S1	8.13 ± 0.04 bc	pH = 1.43 H ⁺ + 8.24	0.8995
C2S2	8.24 ± 0.06 abc	pH = 1.96 H ⁺ + 8.42	0.9514
C2S3	8.25 ± 0.12 abc	pH = 1.52 H ⁺ + 8.41	0.9318*
C2S4	8.43 ± 0.02 a	pH = 1.74 H ⁺ + 8.57	0.9137*
C2S5	8.52 ± 0.01 a	pH = 1.83 H ⁺ + 8.58	0.9368*
C3S1	8.10 ± 0.04c	pH = 1.24 H ⁺ + 8.20	0.9843*
C3S2	8.25 ± 0.10 abc	pH = 1.65 H ⁺ + 8.34	0.9212*
C3S3	8.25 ± 0.09 abc	pH = 1.90 H ⁺ + 8.52	0.9065*
C3S4	8.42 ± 0.01 a	pH = 1.19 H ⁺ + 8.46	0.9672*
C3S5	8.40 ± 0.02 ab	pH = 0.88 H ⁺ + 8.47	0.9779*

Note: Different letters indicate significant mean differences using Tukey's HSD test at $p \leq 0.05$. Data are presented as mean ± standard error of three replicates. R^2 values with an asterisk imply the significant relationship at the confidence level of 95 %.

with high Al and Fe oxides content. This soil is made up of kaolinite clay minerals which are characterized by fine loamy texture, low CEC, and excessively weathered because of high rainfall and hot temperatures throughout the year, thus resulting in low pHBC [54,68]. In contrast, the improved pHBC of the soils with Calciprill and sodium silicate is related to the increased soil pH, ECEC, CaCO₃, and the presence of water soluble Si [76,86]. When the soil pH is approximately 8, the dissolution of CaCO₃ can buffer the soil pH changes when the H⁺ ions are released to the soil solution through the dissolution of acidifying fertilizers and the uptake of base cations by the crop root hairs [9]. In this study, the continued dissolution of the Calciprill to improve pHBC of Bekenu series was possible because the initial pH of the soil with the amendments (C1S1 to C3S5) had the pH of approximately 8

throughout the incubation study (Table 4). The soil with the Calciprill and sodium silicate (C1S1 to C3S5) had significantly higher soil ECEC (Fig. 5), indicating that the amended soils contain the higher number of negatively charged sites to buffer the exogenous H⁺ via cation exchange reactions [71,86].

Besides, the release of exchangeable base cations (K⁺, Ca²⁺, Mg²⁺, and Na⁺) through the dissolution of amendments can rapidly exchange with H⁺ ions in the soil solution, which led to the adsorption and immobilization of H⁺ on the soil exchangeable sites to improve pHBC [11,86]. It is also reported that the incomplete dissolution of Calciprill can slowly neutralize these immobilized H⁺ through continued dissolution over time, thus resulting in improved soil pHBC [14,63]. According to Tubaña and Heckman [76], the inclusion of Si-rich materials can release polysilicic acid which eventually improves soil pHBC through the formation of Si bridges between the soil particles. Additionally, Shi et al. [70] reported that the presence of water soluble Si such as dissociated monosilicic acid (for example H₃SiO₄⁻) in the alkaline soils can react with H⁺ ions in the solution through precipitation to resist soil pH change against the addition of exogenous H⁺ ions.

3.3. Relationship between pH, effective cation exchange capacity, and pH buffering capacity

The pHBC positively correlated with pH at 40 DAI ($r = 0.4055$), 80 DAI ($r = 0.4155$), and 120 DAI ($r = 0.5147$) when Bekenu series was applied Calciprill and sodium silicate (Table 8). In addition, Table 8 demonstrates that soil ECEC positively correlated with pHBC at 40 DAI ($r = 0.4155$), 80 DAI ($r = 0.5507$), and 120 DAI ($r = 0.5543$). At 40, 80, and 120 DAI, soil pH was positively correlated with ECEC when the Bekenu series was added with the amendments (Table 8). These significant positive correlations further validate our findings that, improved pHBC of the soils with Calciprill and sodium silicate relate to improved soil pH and ECEC [46]. This finding is comparable with those of DeMontigny et al. [16] and Billah et al. [8] who reported that the increased soil pH can lead to the improvement of ECEC and surface charge on the soil colloids amended with CaCO₃.

In comparison, regardless of day of incubation, the correlation coefficients between pH and pHBC were consistently higher than those correlation coefficients between ECEC and pHBC, suggesting that the effects of ECEC on improving pHBC of Bekenu series were more pronounced compared with soil pH. This finding is in consonance with that of Zhang et al. [86], who also opined that the results of structural equation model (SEM) showed that the variations of ECEC can significantly and directly regulate pHBC compared with other soil chemical properties such as CaCO₃ and soil organic matter, which indirectly influence the soil pHBC. This is because Aprile and Lorandi [6] reported that the soil CEC is closely correlated with ECEC when the soil pH is greater than 8.3 because the exchangeable acidity is considered negligible in alkaline soils. In alkaline soils, Ranjbar and Jalali [62] also demonstrated that the NH₄⁺ adsorption improves with the significant increase in the soil CEC because of the increasing CaCO₃ content.

The results in our soil incubation study showed that the pH of most of the treatments with Calciprill and sodium silicate had a value of approximately 8.3, regardless of day of incubation. This finding suggests that it is possible that the soils following the combined use of Calciprill and sodium silicate can improve NH₄⁺ adsorption to mitigate rapid nitrification, which could be due to the increased soil CEC. Therefore, these findings indicate that our approach can mitigate the N contamination in water bodies because of improved NH₄⁺ adsorption and reduced nitrification, as reported in our previous papers [47,48].

According to Zhang et al. [86], the significant increase in the soil pHBC because of the improved ECEC is related to the rapid exchange reaction of H⁺ ions with the added base cations such as K⁺, Ca²⁺, Mg²⁺, and Na⁺ when the soil pH is in alkaline range. Moreover, addition of the amendments with higher pH and base saturation compared with the soil does not only improve ECEC, but this approach also

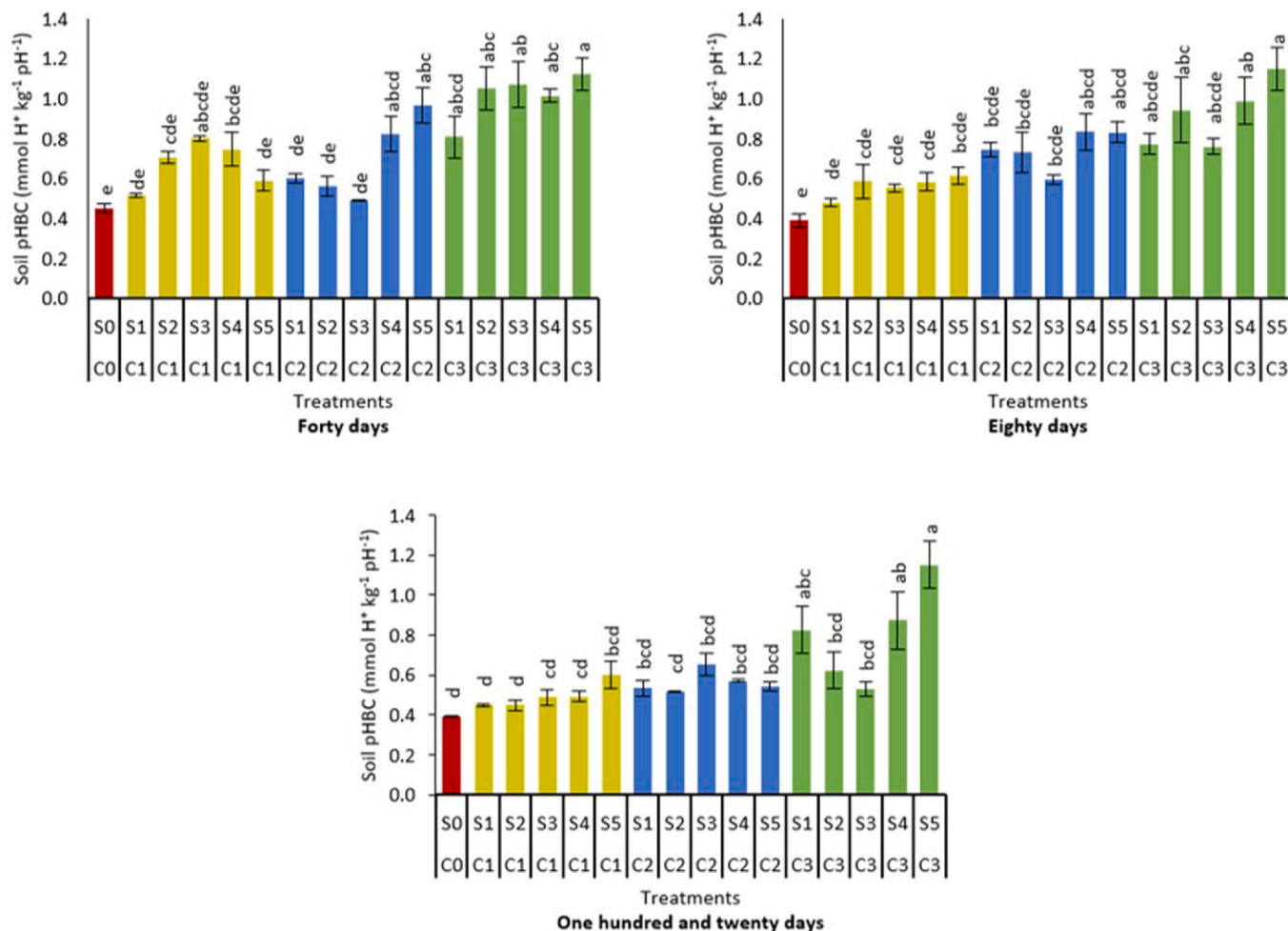


Fig. 5. Soil pH buffering capacity in relation to combined use of Calciprill and sodium silicate at forty, eighty, and one hundred and twenty days incubation. Different letters indicate significant mean differences using Tukey's HSD test at $p \leq 0.05$. The error bars refer to \pm standard error of three replicates.

Table 8
Relationship between pH, effective cation exchange capacity, and pH buffering capacity in the soil co-applied with Calciprill and sodium silicate at forty, eighty, and one hundred and twenty days incubation.

Variables	Days of incubation		
	Forty days	Eighty days	One hundred and twenty days
pH and pHBC	$r = 0.4055^*$ $p = 0.0042$	$r = 0.4155^*$ $p = 0.0033$	$r = 0.5147^*$ $p = 0.0002$
ECEC and pHBC	$r = 0.4120^*$ $p = 0.0036$	$r = 0.5507^*$ $p = < 0.0001$	$r = 0.5543^*$ $p = < 0.0001$
pH and ECEC	$r = 0.9285^*$ $p = < 0.0001$	$r = 0.9044^*$ $p = < 0.0001$	$r = 0.9496^*$ $p = < 0.0001$

Note: The Pearson's correlation coefficient (r) values with an asterisk (*) imply the significant relationship between the variables, whereas p values denote the probability level at $\alpha = 0.05$ (n = 48).

immobilizes H⁺ ions, resulting in improved pHBC [11]. It is speculated that the improved ECEC is related to the addition of Calciprill as CaCO₃ source and the ability of sodium silicate to reduce the soil permeability through the formation of silica gel between the soil pores might have also reduced the dissolution of Calciprill [37]. This finding explains the consistency and durability of Calciprill to buffer more added H⁺ over time, which is demonstrated by the significant positive correlations between the variables at 40, 80, and 120 DAI.

Table 9
Relationship between pH buffering capacity with exchangeable ammonium, available nitrate, and available phosphorus in Bekenu series co-applied with Calciprill and sodium silicate at forty, eighty, and one hundred and twenty days.

Variables	Days of incubation		
	Forty days	Eighty days	One hundred and twenty days
pHBC and NH ₄ ⁺	$r = 0.4522^*$ $p = 0.0013$	$r = 0.3538^*$ $p = 0.0136$	$r = 0.2700^{ns}$ $p = 0.0634$
pHBC and NO ₃ ⁻	$r = 0.0328^{ns}$ $p = 0.8247$	$r = -0.3470^*$ $p = 0.0157$	$r = 0.1241^{ns}$ $p = 0.4005$
pHBC and P	$r = 0.5009^*$ $p = 0.0003$	$r = 0.5222^*$ $p = 0.0001$	$r = 0.1487^{ns}$ $p = 0.3132$

Note: The Pearson's correlation coefficient (r) values with an asterisk (*) imply the significant relationship between the variables, whereas ns indicates the relationship between the variables is not significant at $\alpha = 0.05$. The p values denote the probability level at $\alpha = 0.05$ (n = 48).

3.4. Changes of pH buffering capacity on regulating the availability of soil ammonium, nitrate, and phosphorus

Table 9 demonstrates that the pHBC positively correlated with soil exchangeable NH₄⁺ at 40 DAI ($r = 0.4522$) and 80 DAI ($r = 0.3538$). This finding is related to the significant increase in the soil pH which stimulates the transformation of organic N into inorganic NH₄⁺ via

mineralization [45,84]. Also, this finding suggests that the combined use of Calciprill and sodium silicate can increase the available N for crop uptake, although the EDX analysis revealed that there was no N detected in the chemical composition of both amendments (Table 3). However, there was no significant relationship between the pHBC and exchangeable NH_4^+ at 120 DAI. This is related N immobilization by the microorganisms and NH_3 volatilization where our previous results observed that the soil exchangeable NH_4^+ decreases at 120 DAI compared with 40 DAI and 80 DAI, regardless of treatment [47]. In addition to the absence of black pepper plants as our test crop with low N concentration in the Bekenu series, the available plant N which is not being absorbed by the plants might be lost via immobilization, denitrification, leaching, and NH_3 volatilization [10,23,43].

There was no significant relationship between pHBC and available NO_3^- in the Bekenu series co-applied with Calciprill and sodium silicate (Table 9). On the contrary, at 80 DAI, the pHBC was negatively correlated with the soil available NO_3^- ($r = 0.3538$) and this suggests that the increased soil pHBC in the Bekenu can significantly reduce the leaching of mobile NO_3^- from the crop root zone into surface and underground water bodies because NO_3^- is a negatively-charged ion which is repelled by the soil exchangeable sites because of the columbic repulsive effect [21,85]. The negative correlation between the pHBC and soil available NO_3^- at 80 DAI relate to the ability of the amendments to increase soil pH and ECEC, which increases CEC to retain soil exchangeable NH_4^+ from being transformed into available NO_3^- [2,33]. Thus, this finding indicates that the combined use of Calciprill and sodium silicate could mitigate N contamination in water bodies because of reduced available NO_3^- when the soil pHBC increases. Similar to 40 DAI, there was no significant relationship between pHBC and soil available NO_3^- upon the co-application of Calciprill and sodium silicate at 120 DAI because of N immobilization and NH_3 volatilization.

It is observed that the pHBC positively correlated with soil available P at 40 DAI ($r = 0.5009$) and 80 DAI ($r = 0.5222$) because of the ability of Si released from the sodium silicate to mobilize P from Fe minerals because of the higher affinity of Si to react with the adsorption sites of Fe minerals relative to P [46,66]. Although Liao et al. [35] opined that CaCO_3 alone can significantly reduce P availability in acid soils, the significant positive correlation between pHBC and available P suggests that the sodium silicate might be the amendment which dominantly improves P availability in the treated acid soil compared with the Calciprill. There was no significant relationship between soil pHBC and available P at 120 DAI. This is related to the fact that the excess Ca^{2+} reacted with available P in the soil solution to produce insoluble Calcium phosphate over time [57].

4. Conclusions

It is possible to co-apply Calciprill and sodium silicate to improve soil pHBC of Bekenu series because of their alkalinity and rapid dissolution to neutralize excessive soil acidity, suppress Al and Fe hydrolysis, and immobilize H^+ ions. Both preliminary and soil incubation studies demonstrated that the combined use of Calciprill and sodium silicate was able to improve pHBC of Bekenu series, as the soil pH and ECEC increase. The results from the soil incubation study indicate that C2S4, C2S5, C3S2, C3S4, and C3S5 are the treatments which consistently improve pHBC compared with the soil without any amendment (C0S0). This finding suggests that C2S4 is the minimum amount of the amendments required to improve the pHBC of Bekenu series over time. The positive correlations between pH, pHBC, and ECEC further validate that the improvement of soil pHBC of Bekenu series is due to the significant increase in the soil pH and ECEC. Regardless of day of incubation, compared with the correlations between soil pH and pHBC, the correlation coefficients between ECEC and pHBC were consistently higher, suggesting that ECEC is the factor that dominantly improve soil pHBC. The strong positive correlations between pH and ECEC ($r > 0.90$) at 40 DAI, 80 DAI, and 120 DAI suggests that the increment

of soil ECEC is closely related to the increasing pH when the soil pH is greater than 7 over time. The significant positive correlations between pHBC with exchangeable NH_4^+ and available P at 40 and 80 DAI imply that the Calciprill and sodium silicate can improve NH_4^+ and P availability for crop uptake. Conversely, the significant negative correlation between pHBC and available NO_3^- at 80 DAI suggests that the combined use of amendments can significantly reduce the NO_3^- contamination in water bodies because of improved pHBC, pH, and ECEC. The most suitable combination to improve soil pH, ECEC, and pHBC in this study is C2S4 (Calciprill at 90% Ca saturation and sodium silicate at 135 kg ha^{-1}) and it is possible to co-apply Calciprill and sodium silicate to mitigate NO_3^- in water bodies through leaching and surface runoff. However, the absence of black pepper plant (test crop) in this laboratory assessments did not provide the fundamental information of plant-soil interactions. Therefore, greenhouse study is recommended to further validate the findings in this study.

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CRedit authorship contribution statement

Conceptualization, J.F.N. and O.H.A.; methodology, J.F.N. and O.H.A.; investigation, J.F.N.; resources, A.A.M.; writing—original draft preparation, J.F.N.; writing—review and editing, O.H.A., L.O., A.J.K.C., and M.B.J.; visualization, J.F.N.; supervision, O.H.A., L.O., M.B.J., and Y.M.K.; project administration, O.H.A., L.O., M.B.J., and A.A.M.; funding acquisition, O.H.A., L.O., M.B.J., and A.A.M. All authors have read and agreed to the published version of the manuscript.

Data availability

The data presented in this study are available within the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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