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A laboratory study on the effects of fertilizer addition on mobilization, percolation and leaching of calcium ions in soils of Anuradhapura district

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Abstract

This study aims to investigate the effect of fertilizer addition to limestone soils around Thirappane, in Anuradhapura District. Groundwater is the primary source of freshwater in this area. There is evidence that the degree of hardness of groundwater in the area has increased over the years, probably as a result of long-term and large-scale application of chemical fertilizer. Our results show that the exchangeable and total calcium ion concentrations in the soil of non-agricultural increases with depth of the soil profile, indicating the existence of calcium deposits beneath the soil profile. Columns (Dimensions ~ 4.00 cm^2 x 100 cm) were filled with soil (up to 60 cm height in each column) from the study area and 0.5% (w/w) of nitrogen fertilizers (Ammonium sulfate and urea) were introduced to the columns to study the effects of fertilizers on properties of soil. Deionized water (100.0 mL) was added by using a dropper from the top of each column and it was allowed to pass through the soil at a rate of 1 mL/minute. The highest effect on the calcareous soil was shown by fertilizer containing ammonium sulfate. After running the columns for 30 days, it was observed that the pH of the leachate in the column introduced with urea, had gradually declined while the calcium ion concentration had gradually increased, whereas the pH of the leachate, in the column introduced with ammonium sulfate fertilizer, showed a rapid decrease and the calcium concentration was very high, compared to the control. Total calcium ion concentration had decreased down the soil sample columns while exchangeable calcium ion concentration increased. The pH value had also decreased down the soil profile. This indicates the dissolution of calcium carbonate in the soil due to the increment of acidity. This highlights that mobilization, percolation, and leaching of calcium ions in the soil change with nitrogen fertilizer application, potentially contributing to increased groundwater hardness.

Keywords: Calcareous soil, pH, Calcium ion, Nitrogenous fertilizers

Introduction

Calcium is the most abundant alkali metal ion in soil. In some soils it occurs as limestone deposits. The North Central province of Sri Lanka which is situated in the dry climatic zone, is known to contain lime deposits and reported to be with the highest prevalence of kidney diseases in the country. A high level of calcium ion concentration (more than 120 mg/L) in water is suspected to be one of the reasons for kidney disease (Dissanayake & Iqbal, 2014). The reason behind the high levels of calcium in water is speculated to be a result of excessive use of fertilizer for cultivation. Continuous use of inorganic nitrogen fertilizers increases the acidity of soil that in turn increases the breakdown of limestone present in the soil. Most of the exchangeable calcium ions leach, mobilize, and percolate into the groundwater through the soil increasing the accumulation of calcium ions in groundwater. This research was aimed at studying the effect of nitrogenous fertilizer on limestone in soils of the Anuradhapura District and how it affects the percolation, mobilization and leaching of calcium ions in the soil that can contribute to rising groundwater hardness.

In Sri Lanka, most of the paddy lands and croplands, are located in the dry zone where rainfall is seasonal (Jayathileke & Matsueda, 1992). There are two main cultivation seasons per year namely Yala (March to August) and Maha (September to February) where most of the rain is received during Yala (Gunatilaka & Panabokke, 2008). During dry seasons, availability of water in Anuradhapura area is very limited. As a result, during the dry months of the year, people face a serious shortage of water for domestic, agricultural, commercial, and other purposes. Tube wells with a diameter of 150-200 mm and agro-wells with a diameter of 3-5 m have helped to mitigate the shortage to some extent. Groundwater has been the primary source of water for the majority of people in these areas for household needs. This has led to rapid extraction of groundwater resources. According to reports, the shallow groundwater system in the hard rock areas has a continuous aquifer with a single water table in crystalline rocks, in contrast to separate pockets of groundwater, each with a distinct water table (De Silva, 2005) and the quality of drinking water varies from place to place (Dissanayake & Weerasooriya, 1985; Gunatilaka & Panabokke, 2008; Jayathileke & Matsueda, 1992). With time, hardness of this groundwater has become very high and it has been revealed that calcium ions were the main reason for this hardness.

Generally, calcium ions remain adsorbed onto colloidal particles such as clay. These colloidal particles attract cations, especially hydrogen ions due to their surface negativity. The soil contains a reservoir of mobile cations including calcium, which can be exchanged with hydrogen ions thus increasing the soil acidity (Al-aidi et al., 2014; Kroeck, 2011; Rengel, 1992; Narasimhan, 1998).

The acidity of the soil is known to change (Rengel, 1992) with long-term and large-scale use of chemical fertilizer. The increased acidity causes the degradation of limestone mobilizing the calcium ions and as a result, they leach into groundwater. Fertilizers that contain ammonium ions, sulfate ions, and phosphate ions prompt a major effect on the calcareous soil (Al-aidi et al., 2014; Kroeck, 2011; Rengel, 1992; Narasimhan, 1998). In this study, effects from nitrogenous fertilizers were investigated.

Fertilizers containing ammonium salts are used commercially to provide crops with nitrate ions, an important source of nitrogen for plants. Microbial activities have been shown to increase the acidity of the soil when nitrogenous fertilizer such as urea is introduced (Herren,et al., 2020). Furthermore, it has been recorded that many farmers in this area "lime" (add $Ca(OH)_2$) their lands before cultivation. As a result, the calcium concentration in the soil further increases and farmers are reportedly known to overuse fertilizers too. Many studies have revealed that the calcium ion concentration in the topsoil and the calcium ion concentration of groundwater samples in the area to be high (Abeysingha & Gunapala, 2019). However, studies on the effects of fertilizer addition on leaching, percolation, and mobilization of calcium ions in the soil of the area have not been reported.

Methodology/ Materials and methods

All chemicals used were from recognized chemical supplying companies and the purity of each is as given below. Calcium chloride dihydrate (97.0%), Sulphuric acid (96.5% w/v), Hydrochloric acid (35% w/v, density = 1.18 g mL^{-1}), Sodium hydroxide (97%), Hydrogen peroxide (30% w/v), Ammonia solution (25%, density = 0.91 g mL^{-1}) and Ammonium sulphate.

Flame photometer (Jenway PFP7, UK), flame atomic absorption spectrophotometer (FAA-GBC 5000 Savanta model), balance (Kern EW2200 – 2NM), electric oven (Gallencamp), pH meter (Thermo scientific Orian star- MODEL-A211), thermometer, and centrifuge machine (Yider Technology Co.Ltd. Model DSC-200A-1) were used as instruments.

In this study, sampling was conducted in the vicinity of Thirappane town in the Anuradhapura District. A suitable sampling location was chosen in a home garden, where no fertilizer had been applied to the soil. Using an auger screw, five soil samples were collected from each 30 cm depths up to 150 cm, and another soil sample was collected from the surface layer.

All the samples were air-dried and sifted using a 2 mm diameter net sieve and stored in sealed plastic bags in a cool dry place. The surface soil sample was examined for soil characterizations, including pH, calcium ion concentration, cation exchange capacity, moisture content, organic matter content, and texture. The other five samples were examined for pH and calcium ion concentration.

The soil sample collected for the model studies was air-dried for 1 week. Three glass columns (Area is around 4.00 cm^2 and height is around 100 cm) were prepared to model the natural soil structure and to investigate leaching patterns that occur in the soil. Columns were filled with the original soil sample (60 cm in each column). 0.5% (w/w) of the fertilizer (urea and ammonium sulfate) was introduced to the soil from the top of the column. Then fresh deionized water (100.0 mL) was allowed to pass through the soil (1 mL/minute) by maintaining a constant height (5 cm) of the water column over the soil surface. All experiments were duplicated. The blank (control) was prepared as above without using fertilizer.

A fresh portion of deionized water (100.0 mL) was added by using a dropper from the top of each column and the leachate samples were collected. The leachate volumes and the leached calcium ion concentrations were measured. This process was repeated for 30 days. After 30 days the soil in the column was air-dried and was sectioned into slices of 10 cm. Total calcium concentration was determined by using acid digestion method where H_2SO_4 (0.25 M) and HNO_3 (0.5 M) was used in 1:1 ratio and leachable calcium concentration of each section were determined by suspending soil in ammonium acetate solution (pH 7). The total and leachable calcium concentration values of each section were obtained using the flame photometer.

Results and Discussion

Ammonium salts in commercial fertilizer releases ammonium ions to the soil. These ammonium ions are consumed by fungi, and special bacteria (nitrifying bacteria) oxidizing them to nitrate ions, thus releasing hydrogen ions into the environment (Abeysingha & Gunapala, 2019). Calcium ions and other alkaline elements attached to cation exchange sites of soil particles are mobilized due to these hydrogen ions. Furthermore, limestone and other natural calcium compounds begin to decompose due to the acidity of the soil, leaching calcium ions into the soil solution. Concomitantly, these mobile calcium ions will leach/percolate into groundwater through the soil over time, with the rain and irrigated water, contaminating it (Herren et al., 2020; Abeysingha & Gunapala, 2019).

Table 1 shows the variations of total and exchangeable calcium ion concentration with the pH value downwards the soil profile of non-agricultural land in Thirappane, Anuradhapura District.

Table 1. pH and calcium ion concentration with the sample depth in non-agricultural soil in Thirappane, Anuradhapura District.

Sample depth (cm)	Active acidity (pH)	Exchangeable acidity with NH_4OAc (pH)	Exchangeable Ca^{2+} concentration (mg/L)	Total Ca^{2+} concentration (mg/L)
30	6.79	6.6	224	368
60	7.2	6.71	238	336
90	7.24	6.8	240	288
120	7.34	6.71	288	352
150	7.9	7.09	240	448

Total calcium ion concentrations increase with the depth of the non-agricultural soil indicating the existence of the calcium deposits below the soil surface. Furthermore, pH of the soil decrease with the depth of the non-agricultural soil indicating less acidity in the below soil layers.

The highest effect on the calcareous soil was shown by ammonium fertilizers. After running columns for 30 days, it was observed that the pH in the column prepared with urea reduced slowly and the calcium concentration in the resultant leachate samples was gradually increased. The pH of the column prepared with ammonium sulfate fertilizer showed a rapid reduction and the calcium concentration in the resultant leachate samples were comparatively high. The blank/ control showed a lower amount of calcium concentration in the leachate compared to that of the leachates from columns with fertilizers and pH did not change rapidly as in sample columns (Fig. 1).

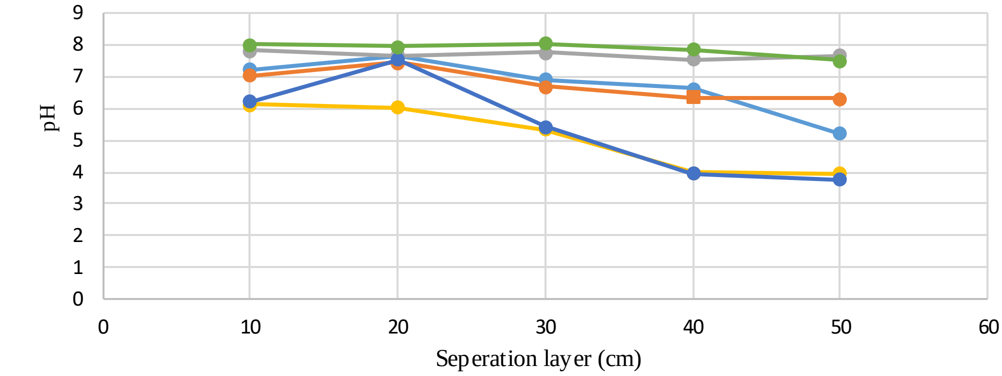

Figure 1. a

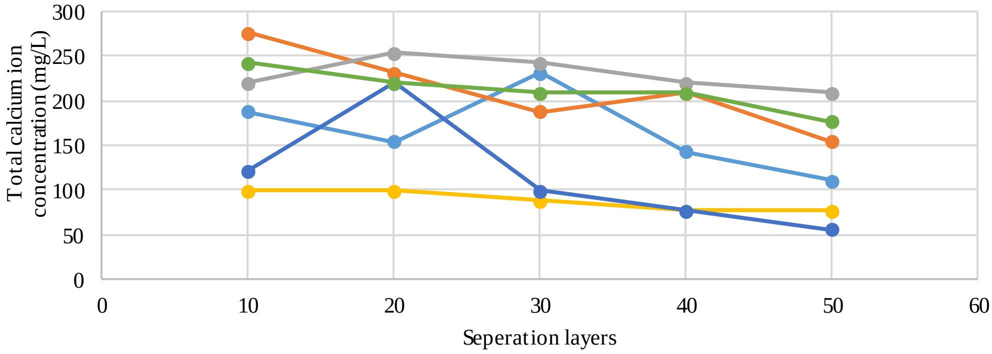

Figure 1. b

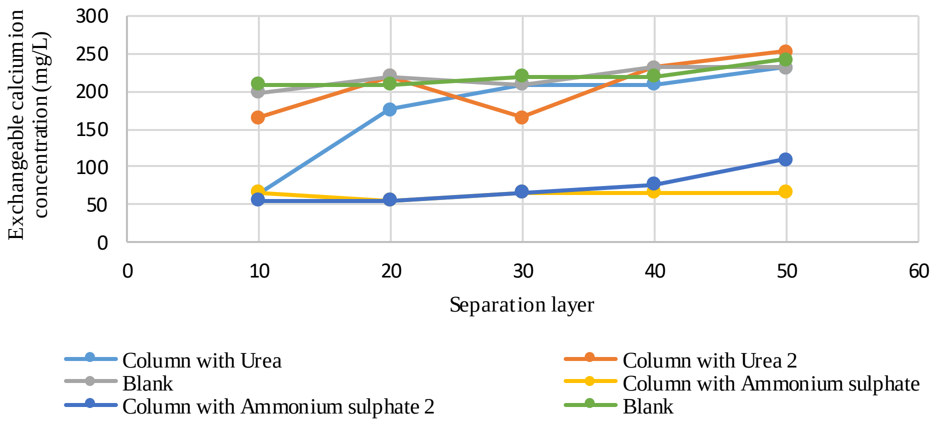

Figure 1. c

Figure 1: Exchangeable and total calcium ion concentration and pH variation down the soil + fertilizer columns.

a) pH variations through the soil column profile.
b) Total calcium ion concentration through the soil column profile
c). Exchangeable calcium ion concentration through the soil column profile.

Total calcium ion concentration was decreased from the top to the bottom of the sample column while exchangeable calcium ion increased in the fertilizer added samples. The pH has also decreased from the top to the bottom through the soil profile. This indicates the dissolution of calcium carbonate in the soil due to the acidification of the soil. Increment of exchangeable calcium ion concentration and the increment of calcium ion concentration in leachate samples in comparison to blanks shows the leaching effects of the calcium ions through the soil. This indicates the effect of nitrogenous fertilizer addition on mobilization, percolation, and leaching of calcium ions in the soil.

According to the observations, the texture of the content of the column which used ammonium sulfate as fertilizers changed rapidly and the water flowing capability through the soil decreased. Soil particles in the columns were observed to accumulate clay and silt particles around them with time. Therefore, this aggregation block the water flow passages. Also it was observed that there was a higher chance of aggregation when ammonium sulfate is used.

Results of the study show that the exchangeable and total calcium ion concentrations in the soil of non-agricultural land increases downwards within the soil profile, which indicate the existence of calcium deposits l below the soil profile. Free or leachable calcium ion concentration increases from the surface to the bottom in soil indicating movement of calcium ions from surface downwards with percolating water. Results of this study therefore support published observations (Paranagama et al., 2018).

Conclusion

According to the results, more calcium ions have been displaced to the leachates as a direct consequence of the nitrogenous fertilizer addition than in the blank samples. It was also observed that the effects of ammonium sulfate are more swift and strong, while the effects of urea are relatively weaker and slower. It can be concluded that this occurs as a result of direct release of ammonium ions from ammonium sulfate, while urea takes longer time to release ammonium ions. Calcium deposits in the soil degrades as the soil becomes acidic due to addition of fertilizers, and the released calcium ions leach into groundwater, increasing the hardness.

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