



Mechanisms for increasing soil resistance to acidification by long-term manure application



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ABSTRACT

Soil pH buffering capacity (pHBC) plays a crucial role in determining soil acidification rates and the amount of lime required to ameliorate soil acidity. However, it remains poorly understood how soil organic matter affects soil pHBC. Here, Alfisol and Ultisol samples from long-term fertilization experiments (control, chemical N, P, and K (NPK), manure only (M), 1/2 NPK plus 1/2 M (1/2NPKM), and NPK plus M (NPKM)) were used to investigate the effects and underlying mechanisms of manure application on the pHBC and soil resistance to acidification through simulated acidification experiments. The results indicated that the application of manure increased pHBC and the resistance of soils to acidification in both the Alfisol and Ultisol. The pHBC of the Alfisol in the M and NPKM treatments was increased by 81 and 60% compared with the control, respectively. Similarly, the pHBC of the Ultisol in the NPKM treatment was 66% higher than that of the control. The extent of protons consumption by the Alfisol followed the order: M > NPKM > 1/2NPKM > NPK ≈ control during stimulated acidification, which was consistent with their pHBC. These results suggested that manure application increased the resistance of the Alfisol to acidification by increasing soil pHBC. The protonation of organic anions from the dissociation of weakly acidic functional groups on soil organic matter to form neutral molecules was the main mechanism responsible for the increase in pHBC and soil resistance to acidification induced by manure application. During this process, some exchangeable base cations were released from negatively charged sites on organic matter into soil solution. This mechanism was confirmed by the experimental observations: the release of base cations from soils increased, while soil exchangeable base cations and effective CEC decreased as soil pH decreased. The results are of fundamental significance for understanding the role of organic matter in retarding soil acidification through long-term manure application.

1. Introduction

Soil acidification has received increasing attention due to the serious threat it poses to agricultural production and biodiversity in terrestrial ecosystems (Chen et al., 2013). As soil acidified, the toxicity of aluminum (Al) and manganese (Mn) to plants and the deficiency of nutrients, such as phosphorous (P), potassium (K), calcium (Ca), magnesium (Mg), and molybdenum (Mo), occurred and thus reduced crop yields and threatened food security. Soil acidification is slow under natural conditions. However, it has been greatly accelerated in recent decades due to acid deposition (Liu et al., 2010; Lawrence et al., 2015; Driscoll et al., 2016) and the excessive application of NH₄⁺-based

fertilizers producing proton through the oxidation of ammonia to nitrate (Zhang et al., 2009; Guo et al., 2010; Gu et al., 2015; Tian and Niu, 2015; Zeng et al., 2017). Soil acidification rate mainly depends on net inputs of acid and soil pH buffering capacity (pHBC) (Brady and Weil, 2010). When the same amount of protons was introduced into soils, the greater soil pHBC led to the slower soil acidification rate. Therefore, improving soil pHBC is an alternative to retard soil acidification for sustainable agriculture apart from reducing acid input into soils, especially for the soils in tropical and subtropical regions. So far, most investigations have focused on ameliorating soil acidity (Li et al., 2015; Shi et al., 2016; Dai et al., 2017), decreasing acidic deposition (Lawrence et al., 2015; Driscoll et al., 2016), and inhibiting proton

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production from synthetic N fertilizers (Masud et al., 2014; Jiang et al., 2014). Feasible measures remain scarce to retard soil acidification through improving soil pHBC (Shi et al., 2017).

Soil pHBC is governed mostly by dissolution/precipitation of carbonates at pH > 6.8, by cation exchange reactions in the soils with intermediate pH (4.5–7.5) and by dissolution/hydrolyzation of aluminum compounds in the soils at pH < 4.5 (Bowman et al., 2008). In addition, the dissolution of clay minerals and primary minerals also contributes significantly to soil pHBC at longer time scales or in soils with high contents of weatherable minerals (Herre et al., 2007; Nelson and Su, 2010). A strong positively linear relationship between pHBC and soil organic matter (SOM) was observed in acidic soils (Weaver et al., 2004; Nelson and Su, 2010; Xu et al., 2012). The decrease in soil pHBC with the increase in depth of soil profile also indicated the importance of organic matter for pHBC (Nelson and Su, 2010). Soil pHBC varied with the changes in the amount or nature of soil organic matter (García-Gil et al., 2004; Nelson and Su, 2010). It was assumed that weakly acidic functional groups such as carboxyl and phenol on organic matter formed a strong buffering system through protonation/deprotonation, which was responsible for the increase in soil pHBC induced by organic matter (Weaver et al., 2004; Xu et al., 2012). However, the above hypothesis about mechanism still needs the experimental verification.

The application of manure is an effective farming practice for increasing the content of soil organic matter (Goss et al., 2013; Yang et al., 2015). The results in previous studies showed that the increase in SOM resulting from the incorporation of manure inhibited soil acidification (Cai et al., 2014, 2015). Conventionally, it was considered that manure application could inhibit soil acidification by the return of base cations into soils (Butterly et al., 2013; Cai et al., 2015), ammonification of labile organic N in manure (Xu et al., 2006), decarboxylation of organic anions (Xiao et al., 2013), and formation of Al-organic matter complexes (Wen et al., 2014; Hagvall et al., 2015; Wang et al., 2016). However, the contribution of manure application to the increase in soil pHBC and thus to inhibit soil acidification has never been evaluated. Up to now, the effects and mechanisms of long-term manure application on increasing soil pHBC and then inhibiting soil acidification have not been investigated yet.

To address this knowledge gap, we collected Alfisol and Ultisol samples from two long-term field experiments, with different fertilization treatments (control, manure only, chemical fertilizers only, and chemical fertilizers combined with manure). A simulated acidification experiment in laboratory was subsequently conducted to determine the role of manure application in retarding soil acidification. Given the significantly positive relationship between soil pHBC and SOM as well as CEC, we hypothesized that (i) manure application would inhibit soil acidification through increasing soil pHBC; (ii) the protonation of weakly acidic functional groups on organic matter is the main mechanism responsible for the increase in soil buffering capacity, which lowers the effective cation exchange capacity (ECEC) and leads to the release of exchangeable base cations. The results obtained from this study will provide useful references for soil acidification retardation by organic manure application, especially for highly weathered soils with a low pHBC.

2. Materials and methods

2.1. Soil samples and fertilization treatments

Two test soils used in this experiment were collected from the South of China in 2015. The Alfisol derived from Triassic limestone and sandy shale was collected from a long-term experimental maize field at Yellow Soil Experimental Station, Guizhou Academy of Agricultural Sciences, Guiyang, Guizhou Province (106°07' E, 26°11' N). The Ultisol derived from Quaternary red earth was collected from a long-term fertilization experiment, with a wheat-maize crop rotation at Red Soil Experimental

Station, Chinese Academy of Agricultural Sciences, Qiyang, Hunan Province (26°45'N, 111°52'E). The long-term Alfisol and Ultisol experiments were established in 1995 and 1990, respectively. Alfisol samples were collected from five long-term fertilization plots: (1) non-fertilization (control), (2) N, P, and K (NPK) chemical fertilizers, (3) cattle manure only (M), (4) 1/2 NPK plus 1/2 M (1/2 NPKM) (50% N from manure, and 50% N from chemical N fertilizer), and (5) total NPK plus total M (NPKM). Ultisol samples were collected from two long-term fertilization plots, a non-fertilization (control) and NPK plus pig manure (NPKM) (70% N from manure, and 30% N from chemical N fertilizer). The chemical fertilizers used in both long-term field experiments were urea, superphosphate, and potassium chloride. The N, P, and K fertilizers were applied to the Alfisol at rates of 330, 72, and 137 kg ha⁻¹ year⁻¹, respectively. The rate of total N in the NPKM treatment was double the amount of N applied in other treatments. In the case of the NPKM treatment for the Ultisol, P and K fertilizers were applied at rates of 53 and 100 kg ha⁻¹ year⁻¹, and the total N applied was 300 kg ha⁻¹ year⁻¹ (70% from manure and 30% from urea). The treatment plots distributed randomly. There were three replicates for each treatment in the both long-term fertilization trials. Five cores of soil samples at 0–20 cm depth were collected from each treatment plot and then they were thoroughly mixed as one composite sample for the treatment. After being air-dried, the soil samples were ground to pass through a 0.25 mm sieve for determining the properties of soil samples and a simulated acidification experiment. The soil pH was determined by an Orion 720 pH meter (Thermo Fisher Scientific, Waltham, MA, USA) in deionized water at a 1:2.5 w/w ratio. Soil organic matter was measured using the dichromate method and soil CEC was determined with the ammonium acetate method at pH 7.0 (Pansu and Gautheyrou, 2006).

2.2. Removal of soil organic matter

To verify the role of soil organic matter in improving the resistance of soils to acidification, the soil organic matter in the Alfisol from the M and NPKM treatments was removed by the H₂O₂ peroxidation method (Zhao et al., 2014). Soil samples (60 g) were placed into 500 mL beakers, and 20 mL of 30% H₂O₂ was added. The suspension was stirred to ensure the reaction proceeded at room temperature. When frothing had completely subsided, the beakers were maintained in a water bath at 75 °C until they were approximately dry. The step was repeated several times until no reaction could be observed. Excess H₂O₂ was expelled by heating at 50 °C. The samples were ground to pass through a 0.25 mm sieve for the following simulated acidification experiments.

2.3. Determination of soil pHBC

Acid-base titration curves are normally used to determine soil pHBC (Luo et al., 2015; Cai et al., 2017). Although the acid-base titration curves of soils were sigmoid in shape over a wide range of pH, the amount of acid and alkali added was linearly related to soil pH in the range pH 4.0–7.0 (Nelson and Su, 2010). The range of pH 4.0–7.0 encompasses most acid agricultural soils. Here, the soil pHBC was calculated from the slope of the linear portion of acid-base titration curves (Xu et al., 2012). In brief, titration curves were established by adding incremental amounts of HCl or NaOH to soil suspensions with a 1:5 solid/liquid ratio. In each titration, soil samples (4 g) were placed into each of ten polyethylene tubes and appropriate amounts of deionized water were added to achieve a final volume of 20 ml after the addition of 0.04 M (standardized) HCl or NaOH. For most soil samples, 0, 0.5, 1.0, 2.0, 3.0, 5.0, and 7.0 mL HCl or NaOH were added. To ensure a pH range of titration curves from 4.0 to 7.0, the addition of HCl or NaOH was adjusted depending on the initial soil pH. To minimize the variations in ionic strength, 1.0 ml of 0.04 M CaCl₂ was added to each tube. To inhibit microbial activity, 0.25 ml of chloroform was added to each tube. The suspensions were shaken for 24 h at 25 °C and equilibrated for

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