Model carbon compounds differ in their effects on pH change of soils with different initial pH

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Abstract

Laboratory experiments were carried out to investigate the mechanisms of soil pH change using organic compounds. Carbon (C) compounds commonly found in plant material (citric acid, ferulic acid, glucose and glucosamine hydrochloride, potassium and sodium citrate) were selected based on the type and number of functional groups and applied to two soils differing in initial pH. Organic acid (R-COOH) addition instantly decreased soil pH via H^+ dissociation followed by an increase in pH through decarboxylation. The ability of soil to return to the original pH was less with increased rate of acid addition and was not restored at the highest addition rates. Organic anions increased pH of both soils. Soil pH increased with increasing proportion of organic anion when organic acids and anions were added together to the soil. Glucose (R-OH) did not significantly change pH. In comparison, glucosamine hydrochloride ($R\text{-}NH_2$) addition had no major effect on soil pH in Frankston soil (initial pH 4.44) as nitrification was inhibited at low pH, whereas in Shepparton soil (initial pH 6.20), pH subsequently decreased due to nitrification. Therefore, the results demonstrated that C compounds in plant material and initial soil pH regulates the direction and magnitude of pH change.

Key Words

Association/dissociation, mineralisation, alkalisation, organic salt, C rates

Introduction

Organic compounds in plant residues may have a substantial effect on soil pH depending on the nature of the chemical functional groups (Rukshana *et al.* 2009). Some functional groups may be the source of H^+ after dissociation and thus acidify soil (Brady and Weil 2002). Others may be basic or neutral. During decomposition of organic matter chemical reactions are related to the quantities and types of organic chemical functional groups and structural components present in organic compounds (Essington 2004). Association/dissociation of protons from organic compounds is an important process resulting in soil pH change (Xu *et al.* 2006). The amounts of H^+ released or consumed by the added organic matter will determine the change in soil pH. The association/dissociation of functional groups of organic matter depends on mean pKa values of the organic matter and initial pH (Ritchie and Dolling 1985; Tang and Yu 1999; Xu *et al.* 2006). Moreover, the proportion of organic compounds in plant residues varies between species (Gunnarsson and Marstorp 2002) and also plant components (e.g. leaves, shoot) (Yan and Schubert 2000). We hypothesized that the change in soil pH after addition of C compounds would be related to the chemical nature of the compounds and, therefore, neutral functional groups (glucose) would not affect pH whereas acidic (R-COOH) and basic N containing ($R\text{-}NH_2$) compounds would significantly change soil pH.

Method

Soils and C compounds

Soils were collected from Frankston (Podosol) and Shepparton (Tenosol), Victoria, Australia (Isbell 1996). Glucose, citric acid, ferulic acid, glucosamine hydrochloride, potassium citrate (K-citrate) and sodium citrate (Na-citrate) were selected as they represent compounds commonly found in plant residues and differ in the type and number of chemical functional groups. Glucose is a simple carbohydrate with neutral OH and CHO groups. Citric acid is low molecular weight organic acid containing acidic carboxyl (R-COOH) functional groups. Glucosamine hydrochloride is a basic nitrogenous compound that contains an amino group ($R\text{-}NH_2$). K-citrate and Na-citrate are organic anions in the salt form. Ferulic acid is a phenolic compound containing hydroxyl and carboxylic groups.

Experiment 1

The aim of this experiment was to investigate soil pH changes by a range of C compounds. Citric acid, ferulic acid, glucosamine hydrochloride and glucose were added to pre-incubated soil at 0.5 g C/kg soil. Soils were thoroughly mixed and 25 g soil was packed into individual plastic cores (bulk density of 1.4 g cm^{-3}) with 3 replicates. The soil cores were transferred into glass incubation chambers (2009) and incubated for 30 days at 25 ^{0}C. Soil water content was maintained at 80% field capacity. At 0, 1, 3, 7, 15 and 30 days, a set of cores was destructively sampled for analysis. Soil pH was determined using moist soil after extraction in 0.01 M $CaCl_2$ (1:5) by shaking end-over-end for 1 h following centrifugation at 3500 rev min^{-1} for 10 min.

Experiment 2

The purpose of this experiment was to determine the change in soil pH by either an organic acid (citric acid) or anion (K-citrate) at different rates of addition during direct shaking with soil for 384 h. Citric acid and K-citrate were added separately at rates of 0, 0.2, 0.5, 1.5 and 3 g C/kg soil into vials containing 5 g soil, adjusted to 25 mL with 0.01 M $CaCl_2$ (1:5). Soil pH was determined at 1, 24, 96, 192, and 384 h using air-dried soil as described above.

Experiment 3

This experiment aimed to simulate the effect of percent dissociation of an organic acid on pH change. Different ratios of organic acid (citric acid) or salt (tri-Na-citrate) were added to pre-incubated soil using stock solutions at a rate of 0.25 g C/kg soil to give acid: salt ratios of 100: 0, 90: 10, 75: 25, 50: 50, 25: 75, 90: 10 and 100: 0. To ensure equal sodium concentration, Na_2SO_4 was added to balance the sodium in each treatment. The incubation procedure and pH determination were performed as experiment 1 except that samples were taken at 2 and 30 d.

Statistical analysis

Results were analysed by analysis of variance (ANOVA) and significant differences (P<0.05) between means were tested using post-hoc Tukey tests using GENSTAT 11th Edition (Lawes Agricultural Trust).

Results

Experiment 1

Addition of organic acid (citric and ferulic acid) to soil instantly decreased pH due to H^+ dissociation (Figure 1). However, the magnitude of the pH decrease was much greater with addition of citric acid compared to ferulic acid. In subsequent incubation, pH slowly returned to the original level as organic anions were decomposed, consuming H^+ ions. Glucose did not significantly change pH as it is a neutral compound. Glucosamine hydrochloride did not change pH immediately after addition to either soil, but in the Shepparton soil, pH decreased over time due to rapid nitrogen mineralisation through adequate conversion to nitrate (data not presented). No effect of glucosamine on pH in Frankston soil was observed due to the inhibition of nitrification. The magnitude of the pH change was greater in the Shepparton soil which was related to its lower buffer capacity than the Frankston soil.

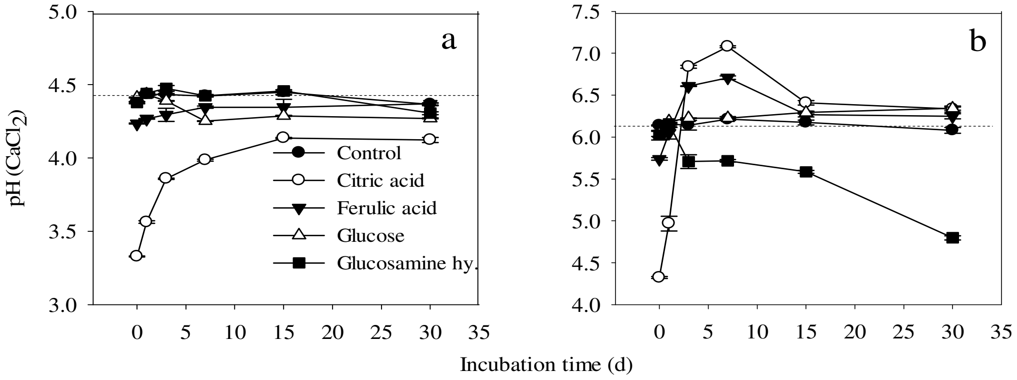

Figure 1. Soil pH changes over a 30 d incubation period after the addition of model C compounds to a) Frankston and b) Shepparton soils. Bars represent the standard error of the mean (n = 3) where they are greater than symbols. Dotted lines indicate the initial pH of the soil (Exp. 1).

Experiment 2

The addition of citric acid immediately decreased pH in both Frankston and Shepparton soils (Figure 2). The magnitude of the soil pH decrease was greater with increased rate of C addition. Over time the pH was slowly restored to the original level and the degree to which pH was restored was less with increased rate of acid addition. Soil pH did not return to the original level at higher rates as H^+ dissociation was much greater than H^+ association. In the Shepparton soil, the magnitude of pH increase was higher over time compared to the Frankston soil.

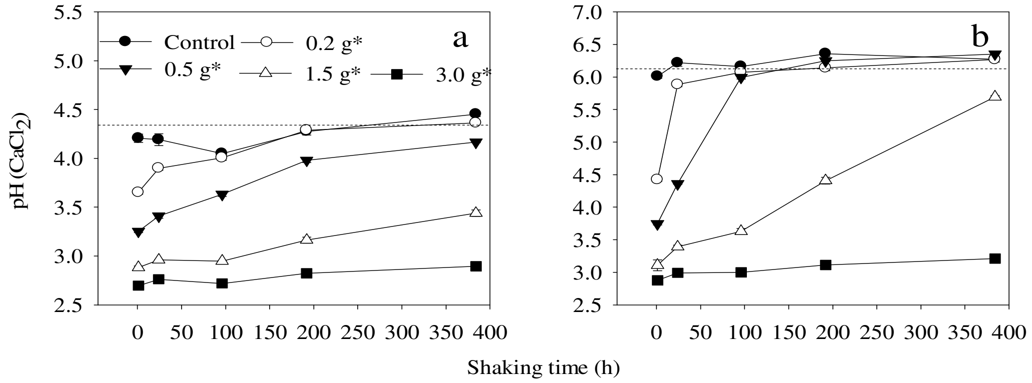

Figure 2. Soil pH changes during 0-384 h shaking after the addition of citric acid at different rates to a) Frankston and b) Shepparton soils. Asterisk (*) specify C/kg soil and bars represent the standard error of the mean, n = 3. Dotted lines indicate the initial pH of the soil (Exp. 2).

In the Frankston soil the addition of K-citrate at rates of 1.5 and 3.0 g C/kg increased pH over time but this was not observed at lower rates (Figure 3). Conversely, in the Shepparton soil pH was greatly increased at the lowest rate of 0.2 g C kg soil compared to the control and there were smaller increases in pH at higher rates of addition compared with the lowest (0.2 g C/kg).

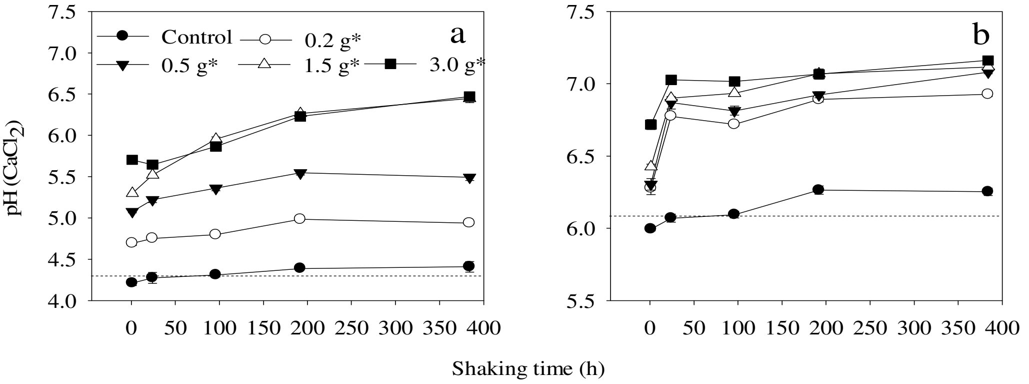

Figure 3. Soil pH changes during 0-384 h shaking after K-citrate was added at different rates to a) Frankston and b) Shepparton soils. Asterisk (*) specify C/kg soil and bars represent the standard error of the mean, n = 3. Dotted lines indicate the initial pH of the soil (Exp. 2)

Experiment 3

Increasing citrate-to-citric acid ratio linearly increased soil pH of the two soils at days 2 and 30 (Figure 4). The pH of the Shepparton soil was higher than the initial pH at 2 d even where 100% citric acid was added. However, in the Frankston soil, pH at day 2 was lower than the initial pH where 50% C was added as citrate. Organic acid addition to soil immediately decreased pH, followed by an increase in pH and magnitude of pH increase was much greater in Shepparton soil compared to Frankston soil. Therefore, at 2 d pH was greater than initial pH in the Shepparton soil and lower than the initial pH in Frankston soil up to a ratio of 50:50. Soil pH increased over time in Frankston soil. However, in Shepparton soil, pH decreased at 30 d compared to 2 d at lower ratios of salt addition (0: 100, 10: 90 and 75: 25) and followed by increasing pH with increasing salt ratio (50; 50, 75: 25, 90: 10 and 100: 0).

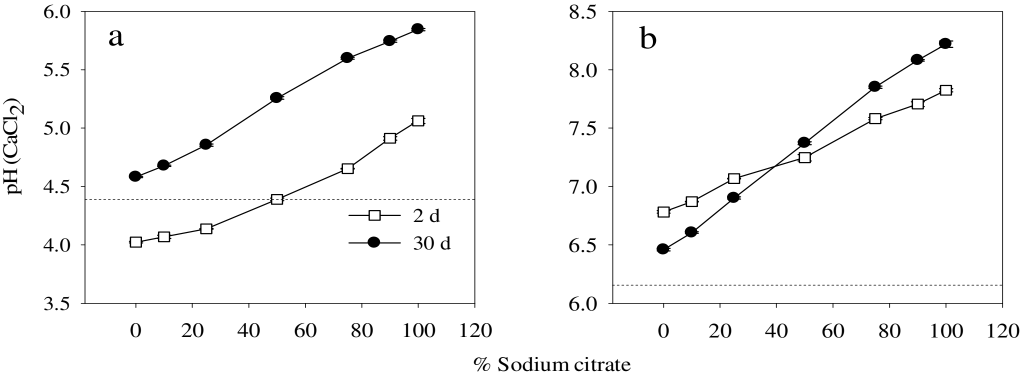

Figure 4. Effect of citrate-to-citric acid ratio on soil pH changes 2 and 30 d after Na-citrate and citric acid were added at a total C rate of 0.25 g/kg to a) Frankston b) Shepparton soil. Citrate: acid ratios are 0: 100, 10; 90, 25: 75, 50: 50, 75: 25, 10: 90, 0:100. The standard error bars were smaller than the symbols. Dotted lines indicate the initial soil pH (Exp. 3).

Conclusions

Organic compounds commonly found in plant residues have significant impacts on soil pH. Organic acids (R-COOH) reduced soil pH immediately after addition to soil due to H^+ dissociation from carboxyl groups followed by an increase in pH due to decarboxylation of the organic anions. Therefore when organic anions (K-citrate) were added to soil, pH immediately increased through decomposition of organic anions. The combined application of organic acid and anion increased soil pH, the pH increase being proportional with increasing organic anion-to-acid ratio. Glucose (R-OH) did not significantly change pH as it is neutral compound. Glucosamine hydrochloride (R-NH_2) decreased pH over time as a result of nitrogen mineralisation through adequate conversion to nitrate (data not presented) in the Shepparton soil. Conversely, glucosamine hydrochloride addition to the Frankston soil had no major effect on soil pH as nitrification was inhibited at low pH. Moreover, the magnitude of soil pH change was greater with increasing rate of C addition. This study showed that the addition of model C compounds to soil can increase, decrease, and did not change pH and the extent and direction of the pH change was associated to the nature, application rate and decomposition of C compounds, and the initial soil pH. Therefore, the composition of C compounds in plant materials will be vital in determining the direction and magnitude soil pH change.

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