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**Abstract** The mechanisms by which organic materials affect soil pH are not fully understood. This study for the first time compared the short-term effect of various model organic compounds on pH change of two soils differing in initial pH (Podosol of pH 4.4 and Tenosol of pH 6.1). Eight organic compounds, representing common compounds in plant residues, were selected based on the number and type of chemical functional groups. The addition of organic acids (acetic, malic, citric and benzoic acid) reduced soil pH immediately due to H<sup>+</sup> dissociation. The magnitude of pH decrease depended on the rate of application, degree of dissociation of the acids and initial soil pH. During a subsequent incubation, pH was slowly restored as these compounds were decomposed. The degree to which pH was restored was reduced with increasing addition rate. The production of H<sup>+</sup> ions was increased with increasing rate of acid addition and decreased over time. When potassium citrate (organic anion) was added, soil pH increased due to H<sup>+</sup> consumption upon decomposition. Compounds with amine groups (glucosamine hydrochloride) and less easily decomposable compounds (phenol) did not significantly alter pH during 16-d shaking. Changes in pH after glucose addition were relatively small compared with other compounds and were not expected because hydroxyl chemical groups of glucose are neutral. The present study demonstrated that the addition of model organic compounds to soil caused soil pH to increase, decrease, or remains unaffected. The extent and direction of pH change was dependent on the chemical functional group, addition rate, decomposition and the initial soil pH.

**Keywords:** Organic compound, plant residues, association/dissociation, initial soil pH, functional group, addition rate, decomposition

## Introduction

Soil organic matter is widely accepted as being central to the sustainability of agricultural production systems via its function in physical, chemical, and biological processes. The influence of organic matter and its cycling on soil pH however, is often unclear with studies reporting increases, decreases or no change in soil pH after the addition of plant residues to soil (Williams 1980; Tang et al. 1999; Tang and Yu 1999; Yan and Schubert 2000; Xu et al. 2006a). The variability in direction and magnitude of pH change may be due to use of different types and amounts of plant material, and the type of soil used.

Soil organic matter is composed of different organic compounds that are generally grouped into following 4 broad classes: carbohydrates; nitrogen compounds; lipids and lignin. Carbohydrates comprise between 5 to 25% of soil organic matter (Essington 2004; Bot and Benites 2005). Cellulose is the principal structural component of plant cells and typically comprises 10 to 50% of plant leaves and approximately 50% of tree wood and bark (Essington 2004). Plants also contribute simple sugars and polysaccharides to the soil environment although these are typically used rapidly by soil microbes. Nitrogen occurs in a great variety of N-containing organic compounds such as amino acids, amino sugars, peptides, proteins, nucleic acids and phospholipids (Mengel 1996; Senwo and Tabatabai 1998; Essington 2004; Jones et al. 2005; Roberts et al. 2007). Lignin is a structural plant component containing phenolic structures and some plant materials may contain up to 6 g phenol kg<sup>-1</sup> fresh weight (Asami et al. 2003). In addition, a number of low-molecular-weight carboxylic acids including malic, citric, oxalic, acetic, succinic, malonic, tartaric, aconitic, formic, pyruvic, benzoic, cinnamic, ferulic, cumaric and vanillic acids (Vickery and Pucher 1940; Shen et al. 1996; Jones 1998; Yan and Schubert 2000; Strobel 2001; Wang and Zhou 2006; Xu et al. 2006b) are commonly found in plant material and soil. Organic acids may play an important role in soil pH change due to the presence of carboxylic structures.

The relative importance of organic matter components to soil pH changes will depend on the content of the organic functional groups capable of releasing or removing protons, and factors controlling association/dissociation reactions. Organic matter components, such as organic acids may be a source of H<sup>+</sup> ions if dissociation occurs (Brady and Weil 2002). However, the association/dissociation of such compounds will depend on the mean acid dissociation constants (pK<sub>a</sub>) of the functional groups present on the organic compounds and the initial soil pH. If the initial soil pH is less than the pK<sub>a</sub> of the acid groups on the added organic compounds, there may be an increase in soil pH due to the association of H<sup>+</sup> from the soil with some of the organic anions and vice versa (Ritchie and Dolling 1985; Tang and Yu 1999; Xu et al. 2006a). The magnitude and direction of pH change can also be affected by soil pH buffer capacity and nitrogen transformation including nitrification.

Since the proportion of different organic compounds (carbohydrate, lignin, etc.) and functional groups (carboxylic, amide, amine, etc.) in plant material varies between species (Gunnarsson and Marstorp 2002), soil pH changes after the addition of plant material will depend on both the type of material and the rate at which it is applied.

Chemical reactions may be accelerated at higher application rates of organic matter to soil. A greater change in soil pH was observed at higher rates of plant residues (Tang et al. 1999; Mokolobate and Haynes 2002) and animal manures (Mokolobate and Haynes 2002; Ano and Ubochi 2007) than lower application rates. Conversely, at high rates of addition, high C:N and nutrient limitation may potentially limit microbial decomposition of the added material (Jenkinson 1977) and thus soil pH may not change.

A number of studies have examined pH changes associated with the addition of plant residues. However, limited information is available on how specific compounds present within these materials contribute to the pH change. Therefore, the aim of this study was to investigate the mechanisms by which different organic compounds alter soil pH and the effects of different C rates on pH in the short-term after application. The experiments described in this paper used a range of organic compounds representing some of the major types of C compounds in plant residues, added at different rates to two soils varying in initial pH. We hypothesized that: 1) acidic functional groups (e.g. citric acid) would initially decrease pH due to H<sup>+</sup> dissociation followed by an increase in pH due to decomposition of organic anions; 2) neutral functional groups (e.g. glucose) would have no effect on soil pH; 3) the magnitude of the acidity/alkalinity change by organic acids would be greater with higher numbers of carboxyl groups even when the same amount of C was added; 4) soil acidity/alkalinity changes would be proportional to the rate of C compound addition.

## Materials and methods

### Soils

Two soils differing in initial pH were collected at 10-30 cm depth (A2) from Frankston (38°14'S 145°22'E) and Shepparton (36°28'S 145°36'E) Victoria, Australia. The soils were then sieved (<2 mm), thoroughly mixed and air-dried for subsequent analysis and incubation studies. These soils are classified as Podosol and Tenosol (Isbell 2002), or Podzol and Cambisol (FAO), respectively, and selected chemical and physical properties of soils are listed in Table 1.

### Carbon compounds

Eight organic compounds (glucose, acetic acid, malic acid, citric acid, glucosamine hydrochloride, potassium citrate, benzoic acid and phenol) 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. Acetic acid, malic acid, citric acid and benzoic acid contain acidic carboxyl (R-COOH) functional groups. The number of carboxyl groups and pK<sub>a</sub> of these organic acids are: acetic acid (pK<sub>a1</sub> = 4.76); malic acid (pK<sub>a1</sub> = 3.4, pK<sub>a2</sub> = 5.13); citric acid (pK<sub>a1</sub> = 3.15, pK<sub>a2</sub> = 4.77, pK<sub>a3</sub> = 6.40) and benzoic acid (pK<sub>a1</sub> = 4.21). Glucosamine hydrochloride is a basic nitrogenous compound (R-NH<sub>2</sub>). Potassium citrate is an organic anion in salt form. Phenol is a phenolic compound with an -OH group and is representative of lignin. Among these, benzoic acid and phenol are aromatic compounds, and others are aliphatic compounds.

### Experiment 1

The objective of this experiment was to determine the temporal changes in soil pH during direct shaking of soil with either an organic acid (citric acid) or anion (potassium citrate) at a wide range of addition rates. Stock solutions of citric acid (72.9 g l<sup>-1</sup>) (BDH Chemicals) and potassium citrate (112.5 g l<sup>-1</sup>) (Chem Supply) were prepared in reverse osmosis (RO) water. Five grams of air-dried each soil was weighed into 50-ml plastic vials (Interpath) and either citric acid or potassium citrate was added at a rate of 0, 0.1, 0.2, 0.5, 1, 1.5, 2 or 3 g C kg<sup>-1</sup> soil using the stock solutions. The final volume of each vial was adjusted to 25 ml with 0.01 M CaCl<sub>2</sub> (1:5 soil: solution) and vials were shaken in an end-over-end shaker at 13 rev min<sup>-1</sup> for 1 h. Soil pH was determined as outlined below. Vials were returned to shaker and this procedure was repeated at 24, 96, 192, and 384 h. Each treatment was repeated three times.

### Experiment 2

This experiment investigated the influence of a wider range of C compounds including glucose (Ajax chemical), acetic acid (Rhone-Poulenc), malic acid, citric acid, glucosamine hydrochloride (Sigma-Aldrich) and phenol (Ajax Finechem) on pH of soil suspension (1:5 soil: 0.01 M CaCl<sub>2</sub> solution) during direct shaking. Stock solutions of glucose (125 g l<sup>-1</sup>), acetic acid (125 g l<sup>-1</sup>), malic acid (139.5 g l<sup>-1</sup>), citric acid (145.8 g l<sup>-1</sup>), glucosamine hydrochloride (149.6 g l<sup>-1</sup>) and phenol (65.3 g l<sup>-1</sup>) were prepared using RO water and added at rates of 0, 0.2 or 0.5 g C kg<sup>-1</sup> soil to individual plastic vials as described above. Benzoic acid (Ajax Finechem) was added to soil as a powder due to its low solubility in water. Soil pH was determined at 1, 24 and 384 h as previously described. The various organic compounds were added to both soils.

### Experiment 3

While Experiments 1 and 2 were conducted using soil suspensions, Experiment 3 was undertaken to examine the effects of an organic acid (citric acid), organic anion (potassium citrate) and a simple sugar (glucose) on soil pH during moist soil incubation. One-hundred grams of air-dried soil was weighed into plastic cups (200 ml), wet to 60% field capacity and placed into incubation chambers as described by Butterly et al. (2009) except that 50 ml of water was added to the base of each chamber to maintain headspace humidity. After pre-incubation for 10 days at 25<sup>o</sup> C in the dark, glucose,

citric acid and potassium citrate were added in solution to the soil at rates of 0, 0.5, 1 or 2 g C kg<sup>-1</sup> soil. The stock solutions of citric acid (243 g l<sup>-1</sup>) and potassium citrate (375 g l<sup>-1</sup>) were adjusted to pH 5.0 using 10 M NaOH and 10 M HCl, respectively. For this, approximate acid-to-anion ratios of 1.5:1 in citric acid and 1:19 in potassium citrate stock solutions were required to bring the citric acid and potassium citrate solutions to pH 5.0. The glucose (208 g l<sup>-1</sup>) stock solution was not adjusted as it was already 5.0. This pH was chosen as it is similar to that of most plant residues (Tang and Yu 1999). Soils within plastic cups were adjusted to 80% field capacity (with gravimetric water content and air-filled porosity of 10% and 0.35 for Podosol, and 14% and 0.28 for Tenosol, respectively), thoroughly mixed and cups were returned to chambers and incubated at 25°C. At the 0 day sampling (4 h after the addition of the stock solutions) soil within each cup was thoroughly mixed and 5 g soil was removed for subsequent pH determination using moist soil. Soils were sampled at 1, 3, 7 and 14 days after incubation; 10 g soil removed and dried at 25°C. To ensure consistent bulk density, the soil remaining in each cup was lightly packed to a uniform height. Soil cups were maintained at gravimetric water content equal to 80% field capacity for the entire period.

#### Analytical procedures

Soil pH was determined using a pH meter (Thermo Orion 720A+, Beverly, MA, USA) after extraction in 0.01 M CaCl<sub>2</sub> (1:5 soil: solution) by shaking end-over-end for 1 h followed by centrifugation at 1507 g for 10 min. Particle-size distribution was analysed following the hydrometer method (Gee and Bauder 1986). The concentration of total C and N were determined using an Elementar Vario EL analyser (Elementar Analysensysteme GmbH, Hanau, Germany). The electrical conductivity (EC) was measured in water extract (1:5 soil: water) with an EC meter (CDM 210, Copenhagen, Denmark). Field capacity was determined using the pressure plate method. Soil pH buffer curves were established between pH 1.8 and 7.8 for the Podosol soil, and 2.1 and 7.8 for the Tenosol soil, by shaking 5 g of soil in 25 ml of 0.01 M CaCl<sub>2</sub> with varying amounts of HCl or K<sub>2</sub>CO<sub>3</sub> for 7 day. The H<sup>+</sup>/OH<sup>-</sup> concentration was estimated based on soil pH buffer curves and pH changes of treated soils against the control soil. Buffer curves for Podosol (1) and Tenosol (2) were described by the following equations:

$$\text{Podosol: } y = -59.794 + 31.46x - 5.477x^2 + 0.318x^3 \quad (1)$$

$$\text{Tenosol: } y = -33.780 + 18.41x - 3.399x^2 + 0.210x^3 \quad (2)$$

where y is the cmol H<sup>+</sup> kg<sup>-1</sup> soil and x is the soil pH.

#### Statistical analysis

For Experiments 1 and 3, three-way analysis of variance (ANOVA) was used to determine the effects of soil × C rate × time using GENSTAT 11<sup>th</sup> Edition (VSN International, Hemel Hemstead, UK). Further two-way ANOVA were performed for each soil using C rate and time as main factors. For Experiment 2, a two-way ANOVA was used with compound and time as the main factors. Significant differences ( $P < 0.05$ ) between means were tested using post-hoc Tukey tests for all experiments.

## Results

### Experiment 1

The addition of citric acid to Podosol and Tenosol soils immediately decreased soil pH (Fig. 1a and 1b). For example, soil pH was reduced by 3.13 units at the rate of 3 g C kg<sup>-1</sup> soil in Tenosol soil compared to the control. Thereafter, the pH slowly increased with time. The increased rate of citric acid addition significantly ( $P < 0.001$ ) decreased pH for both soils. In the Tenosol, pH decreased by 0.92 units at 0.1 g C kg<sup>-1</sup> soil and 3.13 units at 3 g C kg<sup>-1</sup> soil compared to the control. Over time the pH slowly returned to the original level and the degree to which pH was restored was less with increased rate of acid addition. The magnitude of pH change was greater in the higher initial pH soil (Tenosol) than the lower pH soil (Podosol) for the citric acid treatment. Soil pH decreased by 3.13 units in Tenosol and 1.51 units in Podosol compared to the control at a given rate.

The effect of treatments on H<sup>+</sup> production followed the same pattern as that on soil pH but the changes in production of H<sup>+</sup> were approximately double in the lower initial pH soil (Podosol) than the higher initial pH soil (Tenosol) (Fig. 1c and 1d). The H<sup>+</sup> production (negative to OH<sup>-</sup> concentration) was increased by the addition of citric acid and the magnitude increase significantly ( $P < 0.001$ ) greater with increased rate of acid addition. Production of H<sup>+</sup> were 0.69 and 7.84 cmol kg<sup>-1</sup> soil at 0.1 and 3 g C kg<sup>-1</sup> soil, respectively, in Podosol at 1 h. After that the H<sup>+</sup> production reduced over time as decomposition of organic anions consumed H<sup>+</sup>.

Conversely, the application of potassium citrate immediately increased soil pH in both soils and continued to increase over time (Fig. 2a and 2b). In the Tenosol at 24 h, pH increased by 0.94, 1.15 and 1.05 units at potassium citrate rates of 1, 1.5 and 2 g C kg<sup>-1</sup> soil respectively, compared to the control. Although pH continued to increase over time, pH was not different between potassium citrate rates of 1.5 to 3 g C kg<sup>-1</sup> soil after 24 h. However, the magnitude of pH change was greater in the Podosol than in the Tenosol. The pattern of OH<sup>-</sup> production was similar to pH change pattern to both soils. The magnitude of OH<sup>-</sup> was greater in the Podosol compared to Tenosol but the change in OH<sup>-</sup> production over time was greater in the Tenosol (Fig. 2c and 2d).

## Experiment 2

Decreases in pH were observed for a range of organic acids. The magnitude of the pH decrease was in the order of citric acid > malic acid > acetic acid > benzoic acid, except the pH reduction between citric acid and malic acid treatments were not different in the Tenosol. With subsequent shaking, pH slowly returned to the original level in the acid treatments except for benzoic acid in the Tenosol (Table 2). In contrast, initial changes in pH were less after the addition of phenol, glucosamine and glucose to Tenosol and Podosol soils and only slight changes in pH were observed with shaking time.

The magnitude of soil pH change was greater with increased rate of C addition. In the Podosol receiving citric acid, pH decreased by 0.69 units at 0.2 g C kg<sup>-1</sup> soil and 1.15 units at 0.5 g C kg<sup>-1</sup> soil compared to the control (Table 2). After that, pH gradually increased with shaking time and returned to the original level at 0.2 and 0.5 g C kg<sup>-1</sup> soil. Phenol, glucosamine and glucose did not alter pH at either rate compared with the control. Similarly, in the Tenosol soil greater decreases in pH occurred with increased rate of organic acid addition (Table 2), and soil pH values returned to the original level after 384 h of shaking with the exception of benzoic acid (at 0.5 g C kg<sup>-1</sup> soil). For the phenol treatment at 0.2 g C kg<sup>-1</sup> soil, pH was approximately the same after 1 h and 24 h but decreased by 0.53 units after 384 h compared to the control. However, pH was constant during 384 h shaking at 0.5 g C kg<sup>-1</sup> of phenols. With glucosamine, pH increased slightly with shaking time at 0.2 g C kg<sup>-1</sup> soil but was almost constant at 0.5 g C kg<sup>-1</sup> soil. With glucose at 0.2 g C kg<sup>-1</sup>, soil pH increased 0.06 units after 24 h shaking and decreased 0.17 units after 384 h shaking. The same trend was observed with glucose at the rate of 0.5 g C kg<sup>-1</sup>.

Addition of organic acid to soil immediately decreased pH, followed by increased pH over time (Table 2). In Tenosol soil, pH increased by 0.12 and 1.66 units after 24 h and 384 h respectively, when acetic acid was added at 0.5 g C kg<sup>-1</sup>. Moreover, in the Podosol acetic and benzoic acid treatments gradually increased pH between 24 h to 384 h, however a much greater change was observed in the Tenosol soil. In contrast, no major pH change was observed due to addition of the phenol, glucose and glucosamine during the shaking period.

The magnitude of pH change was greater in the higher pH Tenosol soil than the lower pH Podosol soil. In the Tenosol, the reduction in pH after addition of citric acid was approximately double that of the Podosol soil (Table 2).

In general the magnitude of increases in H<sup>+</sup> production was in order of citric acid > malic acid > acetic acid > benzoic acid. Production of H<sup>+</sup> was increased with the increasing rate of acid addition and decreased over time (Table 2). On average, H<sup>+</sup> production was approximately double at 0.5 g C kg<sup>-1</sup> soil than that of 0.2 g C kg<sup>-1</sup> soil, and H<sup>+</sup> production was much greater in the Podosol compared to the Tenosol. Phenol, glucose and glucosamine hydrochloride produced relatively very small H<sup>+</sup>/OH<sup>-</sup> during the shaking period.

## Experiment 3

Incubation of citric acid, potassium citrate and glucose with moistened Tenosol and Podosol significantly ( $P < 0.001$ ) changed pH (Fig. 3a, 3b, 4a, 4b, 5a and 5b). In the Tenosol, citric acid immediately decreased pH by 0.25 units at 0.5 g C kg<sup>-1</sup> soil and 0.87 units at 2 g C kg<sup>-1</sup> soil compared to the control (Fig. 3b) whereas in the Podosol, it increased pH by up to 0.3 units (Fig. 3a). In subsequent incubation citric acid increased soil pH over time with greater increases at higher rates of addition. However, in the Podosol at Day 1 and the Tenosol, soil pH was not further increased at the highest rate (2 g C kg<sup>-1</sup> soil) or was even lower than the treatment of 1 g C kg<sup>-1</sup> soil. Overall similar pH changes were observed for citric acid and potassium citrate treatments in both soils. The magnitude of the pH change was higher in the Tenosol soil than Podosol soil in the citric acid and potassium citrate treatments (Fig. 3a, 3b, 4a and 4b). In comparison, in the glucose treatment (Fig. 5a and 5b) soil pH increased at 1 day after which pH decreased compared at day 1. While soil pH was lower than the control and decreased with increasing rates from Day 7 in the Podosol, it increased with increasing rates except that at Day 14. The effect of glucose on pH change was much smaller (Fig. 5a and 5b) than those of citric acid and potassium citrate.

Production of OH<sup>-</sup> was much lower in the Podosol compared to the Tenosol with the addition of citric acid and potassium citrate (Fig. 3c, 3d, 4c and 4d). In general, OH<sup>-</sup> production increased over time for both soils. Production of OH<sup>-</sup> was not affected by application rate in the Podosol but increased with addition rates up to 1 g C kg<sup>-1</sup> soil to the Tenosol. In Tenosol production of OH<sup>-</sup> was decreased or did not further increase with further increasing rate. In both soils, addition of glucose slightly increased OH<sup>-</sup> production in the first three days but decreased it at Day 14. The magnitude of OH<sup>-</sup> at day 14 increased with increasing addition rate and was greater in Podosol than Tenosol (Fig. 5c and 5d).

## Discussion

The present study demonstrated that the addition of model organic compounds to soil caused soil pH to increase, decrease, or remain unaffected. The extent and direction of the pH change was dependent on the nature, application rate and decomposition of organic compounds, as well as the initial soil pH.

### Chemical functional groups of organic compounds

Organic acids (R-COOH functional groups) reduced soil pH immediately after addition to soil as the concentration of H<sup>+</sup> was increased due to H<sup>+</sup> dissociation from carboxyl groups. Thereafter pH was slowly restored over time as the dissociated organic anion was decomposed consuming H<sup>+</sup> ions and hence, reducing the concentration of H<sup>+</sup> (Experiments 1 and 2). Therefore, we accept our first hypothesis that acidic functional groups initially decreased soil pH

and followed by a subsequent increase in soil pH. When organic anions were added as a salt (potassium citrate), soil pH increased with incubation time as decomposition of organic anions consumed  $H^+$  or produced  $OH^-$  (Experiment 1). However, the incubation study (Experiment 3) showed that the pattern of pH change was similar between citric acid and potassium citrate in both soils. This is likely to be the result of pH adjustment of citric acid and potassium citrate stock solutions to pH 5.0, in which the ratio of organic anion: organic acid was 1:1.5 and 19:1, respectively. Therefore, the citric acid stock solution contained 60% acid form and 40% anion form while potassium citrate stock solution had 95% salt form and 5% acid form. Thus, in the citric acid solution 40% of  $H^+$  ions present on carboxyl groups were substituted by sodium and vice versa in the potassium citrate solution. However, decarboxylation occurred over time consuming  $H^+$ , which increased soil pH.

Aliphatic carboxylic acids are degraded much faster than the aromatic acids which tend to be more stable (Schwab 2000; Marschner and Kalbitz 2003). Therefore, in general  $H^+$  production was greater after addition of citric acid compared to benzoic acid. This study also showed that less easily decomposable compounds (like phenol) did not alter pH during short-term incubation/reactions.

The addition of glucose altered soil pH in this study, which is inconsistent with our second hypothesis that the addition of neutral organic compounds would not influence soil pH. Kemmitt et al. (2006) showed that glucose mineralisation did not contribute to pH change, which may be expected due to neutral chemical functional groups contained within glucose. However, Yan et al. (1996) showed that soil pH slightly decreased at the beginning of incubation with sugar but the effect did not last. In Experiment 3 reported here, the decrease in pH observed at 3, 7 and 14 days in the glucose treatment could be explained by anaerobic breakdown of glucose within soil microsites. Under anaerobic conditions, glucose degradation increase microbial activity through different fermentative microorganisms which produce different organic acids, and eventually decrease in soil pH depending on the glucose addition rate (Chorom and Rengasamy 1997). Glucose-stimulated nitrification is unlikely to be a cause of the pH decline. Our follow-up studies showed that the addition of glucose did not increase the concentration of  $NO_3^-$  in soil (unpublished).

Amine ( $R-NH_2$ ) groups generally alter soil pH through microbial transformation of soil N (Yan et al. 1996; Kemmitt et al. 2006). Transformation of N (organic to inorganic N) via ammonification and nitrification processes is mediated by microorganisms (Bolan et al. 1991). An increase in  $NH_4^+$  concentration in the soil environment increases soil pH and a subsequent conversion to  $NO_3^-$  results in a decrease in pH (Bolan et al. 1991; Xu et al. 2006a; Roberts et al. 2007). Roberts et al. (2007) showed that the addition of glucosamine to soil resulted in rapid N mineralization and subsequent  $NO_3^-$  production. However, in this study glucosamine hydrochloride addition did not change pH in either soil. The disparate findings are probably due to the lack of microbial N transformation at high soil moisture (Brady and Weil 2002). However, nitrogen pools ( $NO_3^-$  and  $NH_4^+$ ) and transformation were not quantified in the current study.

An acid dissociation constant ( $pK_a$ ) of an organic acid indicates the proportion of dissociated and undissociated forms of the organic acid at a given pH. In theory, if the initial soil pH is less than the  $pK_a$  of the organic acid, addition of organic anions may increase soil pH due to association of  $H^+$  from the soil. Conversely, if the initial pH is greater than  $pK_a$  of the organic acid, soil pH may be decreased due to  $H^+$  dissociation (Ritchie and Dolling 1985). In this study, the magnitude of the pH decrease and  $H^+$  production after addition of organic acids were in order of citric acid > malic acid > acetic acid > benzoic acid. The exception was that the magnitude of pH change, and  $H^+$  production, were not differed between citric acid and malic acid treatments in the Tenosol. It is likely that the third  $pK_a$  group ( $pK_{a3}$ ) of citric acid was not dissociated because the  $pK_{a3}$  is greater than the initial pH of the Tenosol. Thus we accept our third hypothesis as the initial change in pH was related to the  $pK_a$  value and number of carboxyl groups when the same amount of C was added. Hence, acids with lower dissociation constants induced a greater decrease in soil pH. Similarly, larger pH decreases were observed for citric acid than succinic acid during a 20-day incubation with three different soils (Li et al. 2008).

#### Addition rate of organic compounds

The magnitude of soil pH changes observed in this study was greater with increased rate of C addition, hence confirming our fourth hypothesis. Soil pH decreased as the addition rate of organic acids (acetic, malic, citric and benzoic acid) was increased, due to the greater dissociation of  $H^+$  at the higher rate than the lower rate. However, in the recovery process, the degree to which the pH was restored to the original level was less at high rates of acid addition due to the greater initial production of  $H^+$  in the soil. When organic anions were added as potassium citrate, soil pH increased with increased application rate and incubation time due to the consumption of  $H^+$  by decarboxylation. Yan et al. (1996) showed that the pH increase was proportional to the amount of  $CO_2$  generated from decomposition of added malate and citrate. However, higher rates of organic anions did not increase soil pH (Experiment 3), which was probably due to the negative impact of high EC on microbial activity and thus decomposition. Higher salinity (EC) reduces enzyme activity (Ghollarata and Raiesi 2007), microbial biomass (Tripathi et al. 2006) and soil respiration (Tripathi et al. 2006; Ghollarata and Raiesi 2007) due to a negative effect on microbial activity. In Experiment 3, EC (1:5 water) increased with increased rate of citric acid (0.23, 0.45 and 0.88  $mS\ cm^{-1}$  at 0.5, 1 and 2  $g\ C\ kg^{-1}$  soil, respectively) and potassium citrate (0.31, 0.66 and 1.37  $mS\ cm^{-1}$  at 0.5, 1 and 2  $g\ C\ kg^{-1}$  soil, respectively) in the Tenosol. At the high rates, EC could be above the critical levels for microorganisms (Yuan et al. 2007), and consequently  $OH^+$  production was decreased with an increase in EC. Therefore, soil pH was not further increased or decreased with further increasing rate (Fig. 3b and 4b).

### Decomposition of organic compounds

Increases in soil pH with increasing incubation time indicate that the effect of organic compounds on soil pH is not only a chemical but also a biological process. Decarboxylation of organic anions is suggested as a major process that increases soil pH (or OH<sup>-</sup> production) after addition of plant material to soil (Yan et al. 1996; Marschner and Noble 2000; Xu et al. 2006a). The effect of decarboxylation on pH will be larger when a greater number of carboxyl groups are present. Organic acids reduced soil pH immediately after they were added to soil due to H<sup>+</sup> dissociation. Then pH slowly increased probably due to decarboxylation where organic anions were decomposed consuming H<sup>+</sup>. Addition of organic acids to soil could have altered pH in two stages: firstly, soil becomes acidified (Stage 1) and after which alkalisation occurs (Stage 2). However, soil pH increased after the addition of an organic anion (potassium citrate) and continued to increase over time. Therefore, net alkalization occurred after the addition of organic anions to soil. Moreover, during the decarboxylation process H<sup>+</sup> consumption will be greater in a soil with higher initial pH than with lower pH due to more favorable pH for microbial activity. However, at high rates of acid addition, the soil initially became more acidified due to the greater concentration of H<sup>+</sup> in the soil which probably inhibited microbial activity and hence decomposition. Therefore, pH did not recover to the original level at higher rates of organic acid addition.

In both soils, the magnitude of the pH change was greater in the incubation study than the direct shaking study at the same addition rate of acid, anion or neutral organic C compounds. This indicates that microbial activity, and thus decomposition, was greater during moist incubation. At a given rate, the pH of soil suspension with addition of organic acids recovered approximately to the original soil pH, while pH of the same treatment in the incubation study was much greater than the original pH.

### Effect of initial soil pH

Previous studies have shown greater changes in soil pH after the addition of plant residues to soils with a lower initial pH than in soils with a higher initial pH (Ritchie and Dolling 1985; Tang and Yu 1999; Xu et al. 2006a). However, in the current study a greater magnitude of pH change occurred in soil with a higher initial pH (Tenosol) rather than a lower initial pH (Podosol). This can be explained by the production of H<sup>+</sup>/OH<sup>-</sup> after the addition of organic compounds and the difference in pH buffer capacity (pHBC) of the two soils. The addition of organic acids to soil immediately decreased pH due to dissociation of H<sup>+</sup>. The amount of H<sup>+</sup> production was much greater in the Podosol (7.84 cmol kg<sup>-1</sup>) than Tenosol (3.63 cmol kg<sup>-1</sup>) at the rate of 3 g C kg<sup>-1</sup> citric acid addition at 1 h (Experiment 1). In addition, the greater magnitude of pH restore (increase) in the Tenosol than in the Podosol might have resulted from a limited decarboxylation in the Podosol as microbial activity and organic matter decomposition could be limited at low pH (Motavalli et al. 1995; Kemmitt et al. 2006; Xu et al. 2006a). Similarly, Li et al. (2008) found greater decreases in pH in soils with high initial pH soil compared with low initial pH soils after the addition of citric and succinic acid.

### Conclusions:

Organic compounds and their rate of addition had a great impact on soil pH change. The present study showed that the extent of soil pH change after addition of these compounds depended on their chemical nature, rate of addition, degree of decomposition, and the initial soil pH and pH buffer capacity. Figure 6 summaries possible mechanisms by which organic compounds affect soil pH. Organic acids reduced soil pH immediately after they were added to soil due to H<sup>+</sup> dissociation and subsequently increased pH due to decarboxylation of organic anions. The magnitude of the pH decrease was greater with increasing rate and number of carboxyl groups. However, in the recovery process pH did not recover at higher rates of addition due to the large production of H<sup>+</sup> in the soil. Moreover, potassium citrate (as an organic anion) increased soil pH through time due to decarboxylation of the organic anions consuming H<sup>+</sup>. Compounds with hydroxyl (glucose) and amine (glucosamine hydrochloride) groups and less easily decomposed compounds (phenol) did not significantly alter pH during short-term incubation. In addition, soil pH was much greater than the original level in the incubation study than direct shaking study. The results indicated that the chemical nature of organic compounds in plant materials and their rate of addition are important in determining the direction and magnitude of soil pH change.

The results have important practical implications. Where crop residues are incorporated into soil at sowing, initial increases in pH resulting from release and decomposition of soluble carboxylates in the residues will create a narrow window for seed germination and seedling establishment in acid soils. The C rates used in this study are comparable to those of crop residues in farming systems. As stated above, the composition of crop residues is very diverse. Apart from carboxylates in both soluble and insoluble forms, there are nitrogen compounds, lipids and lignin. The overall effect of a crop residue on soil pH depends on the chemical composition, decomposability, N and C transformation of the residue. The acidifying effect resulting from nitrification may counteract the alkalization effect of the decarboxylation. Our previous study suggests that the soluble fraction of crop residues contributes up to half of total residue alkalinity within two weeks (Butterly et al. 2009). Future research is warranted to determine the long-term effect of crop residue addition on changes of soil pH, and how these changes affect crop performance.

### Acknowledgements

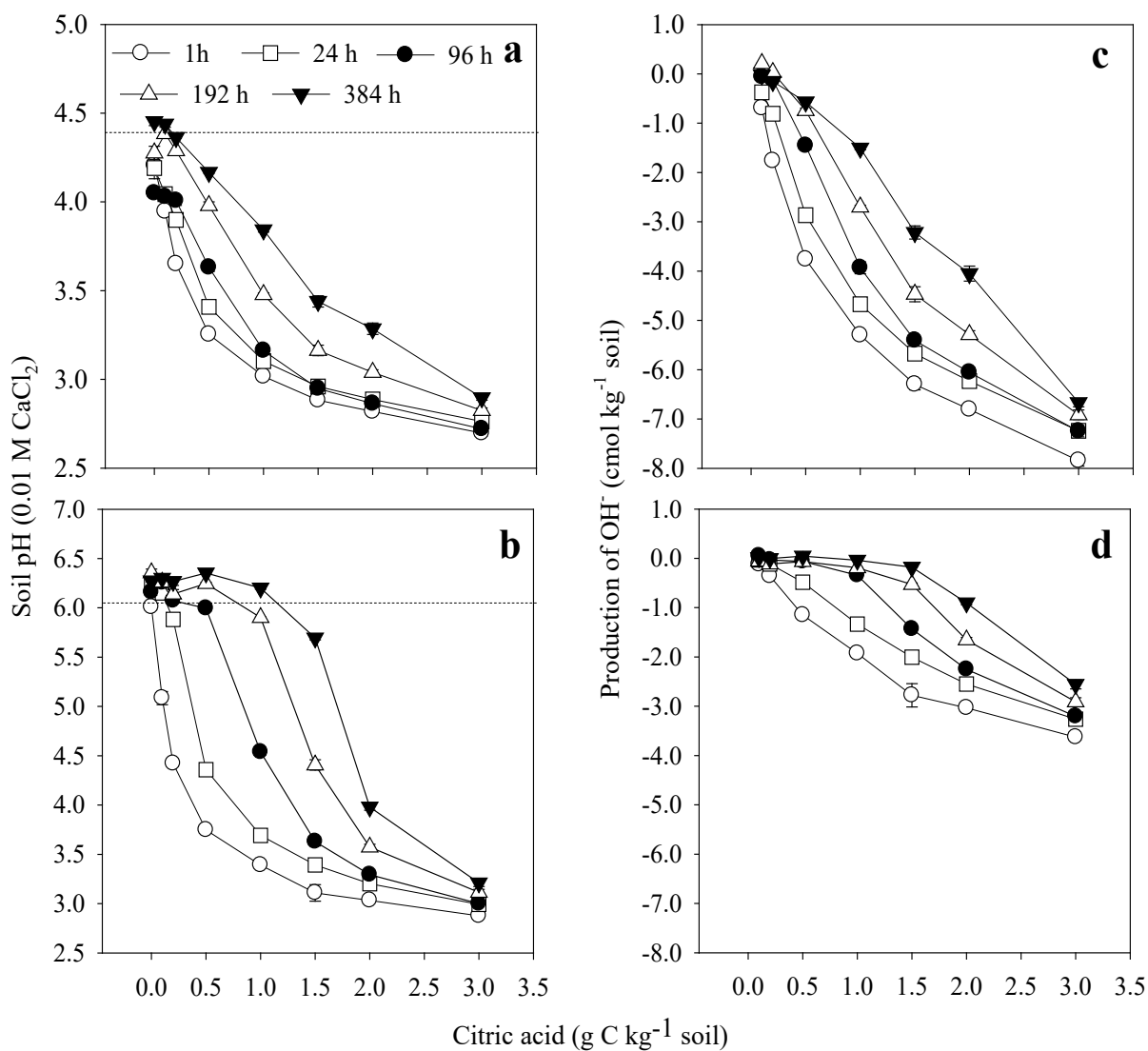
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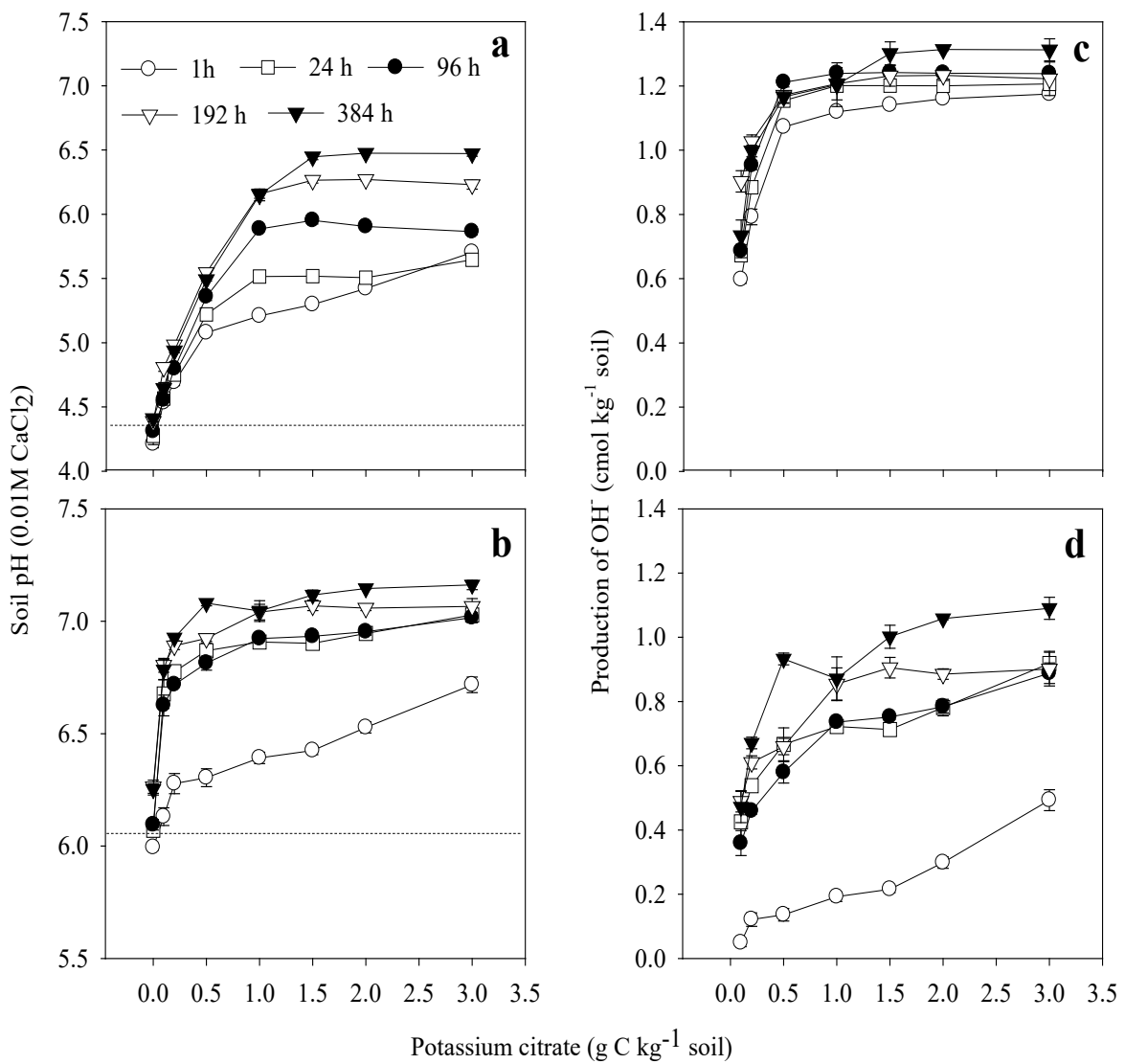
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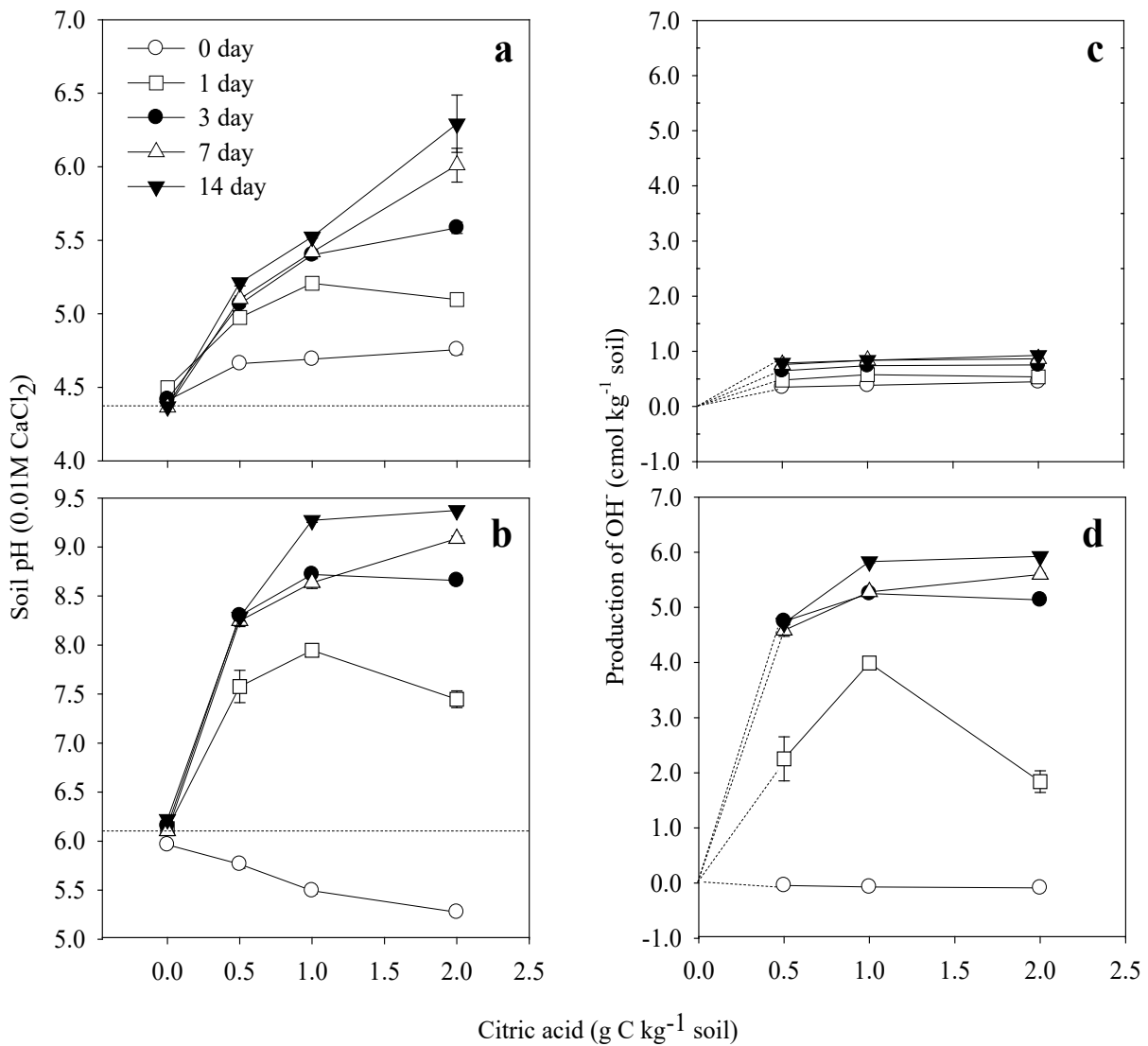




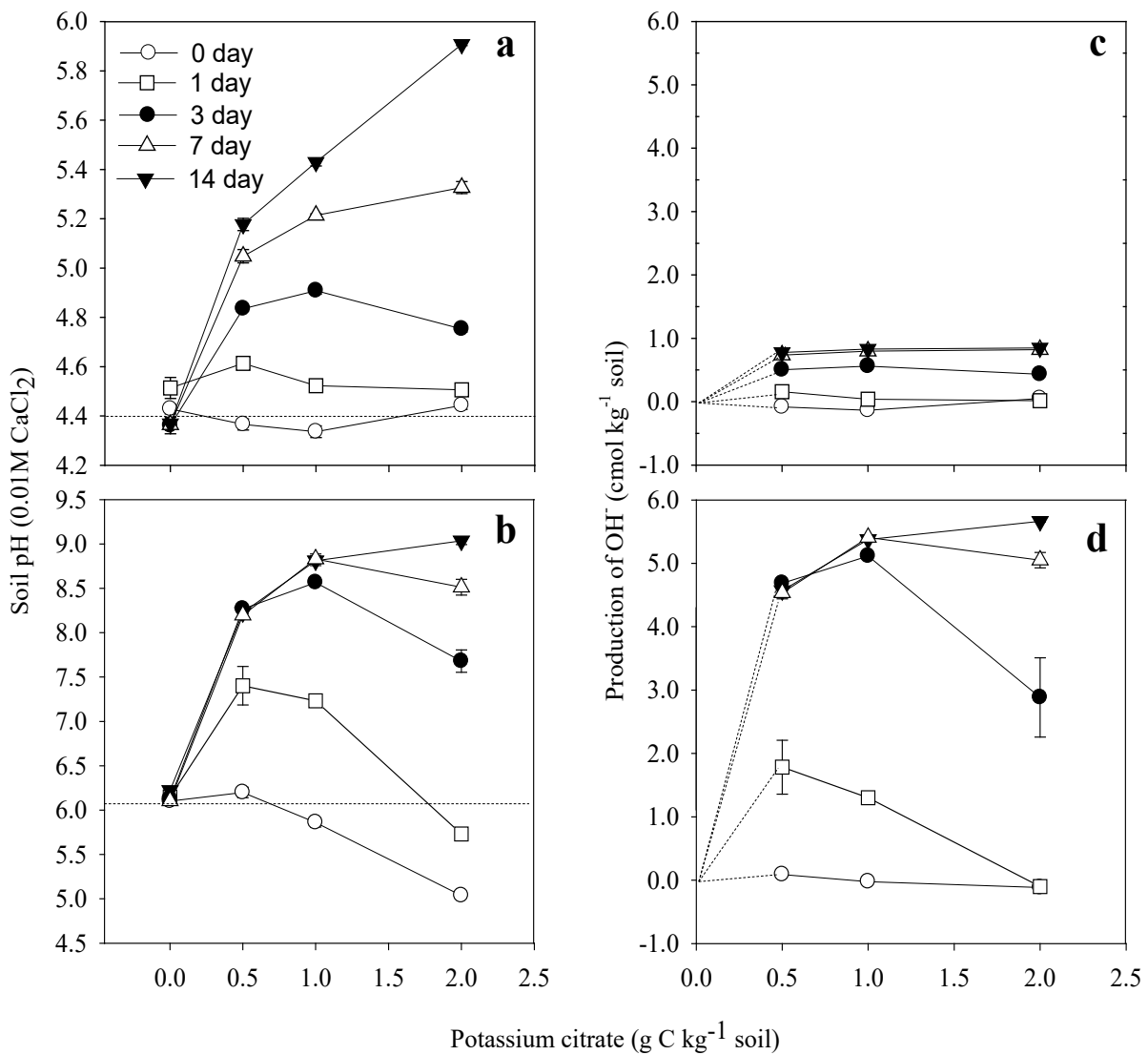
**Fig. 1** Soil pH (a and b) and OH<sup>-</sup> production (c and d) during 0-384 h shaking after the addition of citric acid at different rates to Podosol (a and c) and Tenosol (b and d) soils. Negative values indicate net H<sup>+</sup> production. Bars represent the standard error of the mean (n = 3) where they are greater than symbols. Dotted lines indicate the initial soil pH. Main effects of rate and time, and their interactions were all highly significant ( $P \leq 0.001$ ) (Exp. 1).



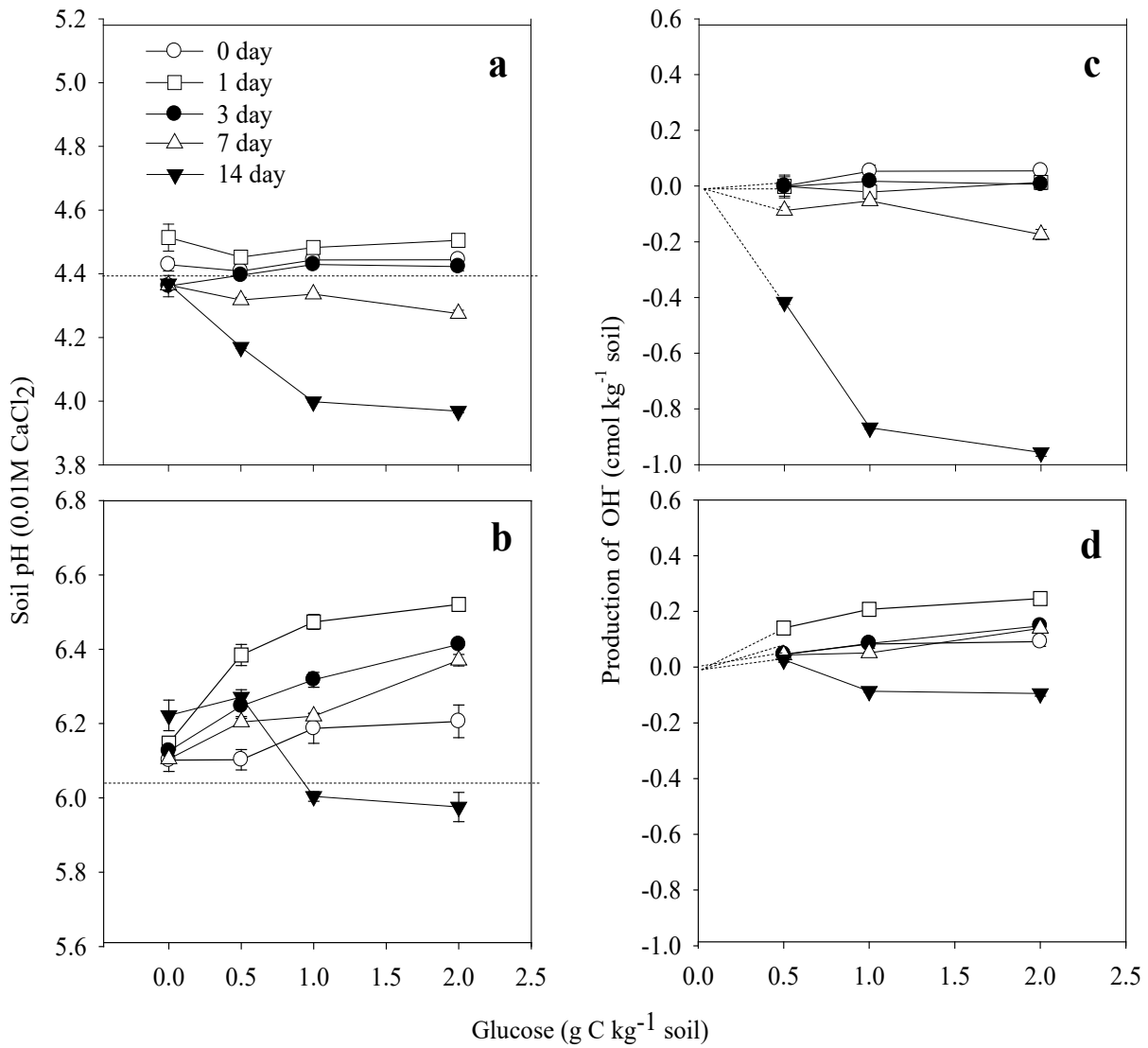
**Fig. 2.** Soil pH (a and b) and OH<sup>-</sup> production (c and d) during 0-384 h shaking after the addition of potassium citrate at different rates to Podosol (a and c) and Tenosol (b and d) soils. Bars represent standard error of the mean (n = 3) where they are greater than symbols. The Dotted lines indicate the initial soil pH. Main effects of rate and time, and their interactions were all highly significant ( $P \leq 0.001$ ) (Exp. 1).



**Fig. 3.** Soil pH (a and b) and OH<sup>-</sup> production (c and d) during 0-14 day incubation after the addition of citric acid at different rates to Podosol (a and c) and Tenosol (b and d) soils. Negative values indicate net H<sup>+</sup> production. Bars represent the standard error of the mean (n = 3) where they are greater than symbols. Dotted lines indicate the initial soil pH. Main effects of rate and time, and their interactions were all highly significant ( $P \leq 0.001$ ). The citric acid stock solution was adjusted to pH 5.0 with approximate acid-to-anion ratio of 1.5:1 (Exp. 3).



**Fig. 4.** Soil pH (a and b) and OH<sup>-</sup> production (c and d) during 0-14 day incubation after the addition of potassium citrate at different rates to Podosol (a and c) and Tenosol (b and d) soils. Negative values indicate net H<sup>+</sup> production. Bars represent the standard error of the mean (n = 3) where they are greater than symbols. Dotted lines indicate the initial soil pH. Main effects of rate and time, and their interactions were all highly significant ( $P \leq 0.001$ ). The potassium citrate stock solution was adjusted to pH 5.0 with an approximate anion-to-acid ratio of 19:1 (Exp. 3).



**Fig. 5** Soil pH (**a** and **b**) and OH<sup>-</sup> production (**c** and **d**) during 0-14 day incubation after the addition of glucose at different rates to Podosol (**a** and **c**) and Tenosol (**b** and **d**) soils. Negative values indicate net H<sup>+</sup> production. Bars represent the standard error of the mean (n = 3) where they are greater than symbols. Dotted lines indicate the initial soil pH. Main effects of rate and time, and their interactions were all highly significant ( $P \leq 0.001$ ). The pH of the stock solution of glucose was adjusted to 5.0 (Exp. 3).

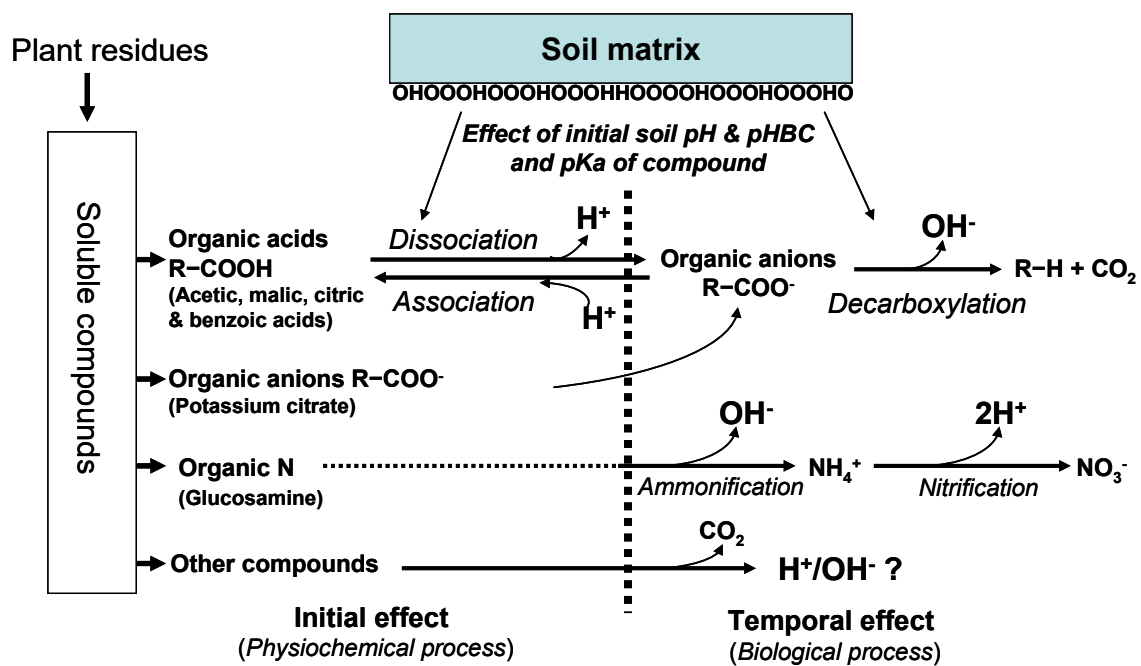


Fig. 6. A conceptual model showing the possible mechanisms of pH changes after the addition of model compounds.

**Table 1.** Selected physiochemical properties of the soils used in the study

Soil type (Isbell 2002)	Soil type (FAO)	pH (0.01M CaCl <sub>2</sub> )	Field capacity (% w/w)	Sand (g kg <sup>-1</sup> )	Silt (g kg <sup>-1</sup> )	Clay (g kg <sup>-1</sup> )	Total C (g kg <sup>-1</sup> )	Total N (g kg <sup>-1</sup> )
Podosol	Podzol	4.5	12	948	2	50	2.89	0.11
Tenosol	Cambisol	6.2	18	881	39	80	1.90	0.21

**Table 2.** Soil pH and H<sup>+</sup> production at 1, 24 and 384 h after addition of model organic compounds to the Podosol soil at 0.2 and 0.5 g C kg<sup>-1</sup>. H<sup>+</sup> production was calculated from the pH buffer curve and pH change of the treated soil against the control soil. The main effects and interactions of organic compound and shaking time on pH and H<sup>+</sup> production are all highly significant ( $P \leq 0.001$ ) for both soils.

Soil	Compound	pH						H <sup>+</sup> production (cmol kg <sup>-1</sup> soil)					
		0.2 g C kg <sup>-1</sup>			0.5 g C kg <sup>-1</sup>			0.2 g C kg <sup>-1</sup>			0.5 g C kg <sup>-1</sup>		
		1 h	24 h	384 h	1 h	24 h	384 h	1 h	24 h	384 h	1 h	24 h	384 h
Podosol	Control	4.46	4.47	4.57	4.45	4.47	4.61	-	-	-	-	-	-
	Acetic acid	4.23	4.28	4.42	4.10	4.17	4.34	0.44	0.35	0.24	0.74	0.60	0.39
	Malic acid	3.89	4.04	4.46	3.51	3.66	4.21	1.35	0.92	0.19	2.85	2.24	0.67
	Citric acid	3.77	4.01	4.46	3.31	3.47	4.21	1.79	0.99	0.18	3.94	3.10	0.67
	Benzoic acid	4.24	4.31	4.47	4.15	4.23	4.42	0.40	0.28	0.16	0.61	0.45	0.26
	Phenol	4.47	4.46	4.60	4.46	4.47	4.60	-0.02	0.01	-0.01	0.00	0.00	-0.02
	Glucosamine	4.47	4.40	4.43	4.44	4.45	4.60	-0.01	0.11	0.27	0.02	0.03	-0.01
	Glucose	4.46	4.45	4.54	4.45	4.46	4.56	-0.01	0.03	0.06	0.01	0.02	0.04
	LSD ( $P=0.05$ )		0.12			0.06			0.20			0.15	
Tenosol	Control	6.28	6.39	6.37	6.23	6.27	6.30	-	-	-	-	-	-
	Acetic acid	4.68	4.82	6.14	4.30	4.42	6.08	0.32	0.32	0.10	0.55	0.51	0.12
	Malic acid	4.43	4.90	6.19	3.78	3.94	6.19	0.45	0.30	0.08	1.21	0.99	0.12
	Citric acid	4.45	5.75	6.17	3.80	4.38	6.24	0.44	0.20	0.09	1.16	0.53	0.06
	Benzoic acid	5.05	5.39	6.06	4.57	4.79	5.89	0.23	0.24	0.13	0.37	0.33	0.18
	Phenol	6.29	6.31	5.84	6.28	6.37	6.37	-0.02	0.01	0.19	-0.02	-0.03	-0.02
	Glucosamine	6.15	6.25	6.35	6.40	6.44	6.35	0.05	0.05	-0.01	-0.09	-0.08	0.22
	Glucose	6.21	6.27	6.10	6.22	6.28	5.95	0.02	0.04	0.11	0.02	0.03	0.17
	LSD ( $P=0.05$ )		0.14			0.17			0.05			0.15	