Chemical mechanisms of soil pH change by agricultural residues

Clayton Butterly[A], Jeff Baldock[B] and Caixian Tang[A]

[A]Department of Agricultural Sciences, La Trobe University, Melbourne 3086, Australia, Email C.Butterly@latrobe.edu.au; C.Tang@latrobe.edu.au
[B]CSIRO Land and Water, PMB 2, Glen Osmond 5064, Australia

Abstract

This paper reports the latest findings from studies on the role of organic matter in soil pH change. Soil pH changes induced by canola, chickpea and wheat residues in two soils with different initial pH (pH 4.4 and 6.2) were investigated under field conditions over 18 months. Changes in pH were related to ash alkalinity however, the relative contribution of canola residue to pH increase was greatly reduced at low initial pH. Furthermore, even at 2 months residue alkalinity had moved down the soil profile, particularly for chickpea. A subsequent incubation study examined the effects of separate soluble and insoluble fractions of these residues. The soluble fraction was the source of alkalinity within the first 2 days. For chickpea the increase in pH by the soluble fraction was greater than whole residue at 2 days however, this fraction subsequently acidified soil possibly due to nitrification of soluble N. These data highlight the need for a better understanding of residue chemistry and the interactions with the soil environment in order to predict the changes in chemical properties such as pH.

Key Words

pH, agricultural residues, organic matter, soluble alkalinity

Introduction

Soil acidification remains one of the key issues facing agricultural productivity and sustainability in Australia and around the world (Kochian *et al*., 2004). Agricultural residues and other plant materials can have a liming effect when added to soil in the absence of plants and leaching (Sakala *et al*., 2004; Tang *et al*., 1999; Tang and Yu 1999; Xu *et al*., 2006b). However, the chemical mechanisms for pH change by agricultural residues are not fully understood. While the quantity and timing of residue application is largely dictated by the farming system and the growing season, agricultural residues may be important for the development of pH gradients within soil profiles.

Increases in pH after the addition of residues are purported to occur due to the decarboxylation of organic anions (Tang and Yu, 1999; Yan *et al*., 1996). Other studies have suggested that basic cations which are released during decomposition increase the pH (Noble and Randall, 1999; Pocknee and Sumner, 1997), however experimental evidence for this does not exist. In fact, Yan and Schubert (2000) showed that the addition of cations as salts (e.g. Na_2SO_4) did not have the same liming effect as sodium malate. Nitrogen (N) cycling is considered a main mechanism for pH change, with the conversion of organic N to NH_4^+ consuming H^+ and subsequent conversion to NO_3^- releasing $2H^+$ (Xu *et al*., 2006a; Xu and Coventry, 2003). Leaching of nitrate results in net acidification and would otherwise be balanced by nitrate uptake by the plant. Furthermore, association/dissociation reactions of H^+ with residue surfaces, organic compounds and the soil matrix may also occur and will contribute to the pH change.

The net effect of these processes will be determined by the soil environment and the chemical composition of the residues. The excess cation content, indicative of ash alkalinity, represents the liming potential of residues (Noble *et al*., 1996). The temporal release of this alkalinity is largely controlled by edaphic factors such as initial pH, cation exchange capacity, organic matter content and texture which influence association / dissociation reactions and biological activity. In addition, microbial decomposition of residues is negatively correlated with C: N and is also inhibited in soils with low initial pH. The concentration and forms of N within residues will dictate the fate of N (mineralisation / immobilisation) and whether the N cycle results in acidification. Furthermore, chemical composition is also important since a high proportion (~50%) of alkalinity in plant materials is potentially immediately available (Sakala *et al*., 2004) and also soluble (Yan and Schubert, 2000) and may have the ability to move through the soil profile.

The aim of our recent experiments reported here was to investigate the role of organic matter in soil pH change in agro-ecosystems. In particular, we used both field and laboratory studies to (i) investigate soil pH changes after residue addition under field conditions, (ii) quantify the contribution of soluble and insoluble residue fractions and (iii) evaluate the proposed mechanisms of pH change including the role of organic N mineralisation, initial soil pH, the chemical nature of residues (particularly C: N and excess cations) and decomposition rate. This paper highlights the main findings of two experiments.

Methods

Experiment 1

A field study was established in 2008 to examine pH changes after residue addition under field conditions. Two soils were collected from Victoria, a Podosol (Isbell, 1996) with a pH of 4.45 from Frankston (38°14'S 145°22'E) and a Tenosol (Isbell 1996) with a pH of 6.20 from Shepparton (36°28'S 145°36'E). Residues of field-grown canola, chickpea and wheat were collected, finely ground and incorporated at 1% w/w into the 0-10 cm layer of soil cores (30 cm long; 10 cm diameter). A set of cores was removed and destructively sampled at 5 times over 18 months. At each time, cores were sectioned into a range of depths and changes in pH (1:5 0.01M $CaCl_2$) and N form and pH buffer capacity were determined.

Experiment 2

A laboratory incubation study was established to determine the contribution of soluble and insoluble fractions of canola, chickpea and wheat to soil pH change. Finely ground residues of canola, chickpea and wheat (termed 'whole') and their fractions were added at 1% w/w to Frankston and Shepparton soils (outlined above). Fractionation of whole residues was performed using reverse osmosis water (1:10) at 70°C for 1 h, followed by centrifugation at 3700 *g* and filtration (Whatman #1). The 'insoluble' fraction was resuspended and extracted a second time and filtered extracts, termed the 'soluble' fraction, from each extraction were combined. Residues and their fractions were mixed separately with pre-incubated soils, packed into soil cores (25 g), placed in gas-tight chambers (Butterly *et al*., 2009b) and incubated at 25°C. Measurements were taken as described above.

Results

Experiment 1

Chemical properties of the residues are outlined below (Table 1). Soil pH changes were related to the alkalinity content of the residues (excess cation content), as illustrated in the Frankston soil (Figure 1). At 2 months after the residues were added, most of the alkalinity had been released (data not shown). The change in pH was attributed to the decarboxylation of organic anions. Alkalinity release from the added residues was reduced in the acidic Frankston soil compared to Shepparton soil, highlighting the importance of initial pH (Xu *et al*., 2006a; Xu *et al*., 2006b). Furthermore, the relative contribution of canola was different between soil types and highlights the important interactions between residue chemistry and the soil environment. This study also showed that some of the alkalinity within chickpea moved down the soil profile over the 2 month period. While to a lesser extent, canola and wheat residues also significantly increased the pH in the soil layer below they were added.

Table 1. Chemical properties of the residues.

Residue	C:N ratio	Ash Alkalinity (cmol/kg)
Chickpea	21:1	150
Canola	40:1	130
Wheat	64:1	45

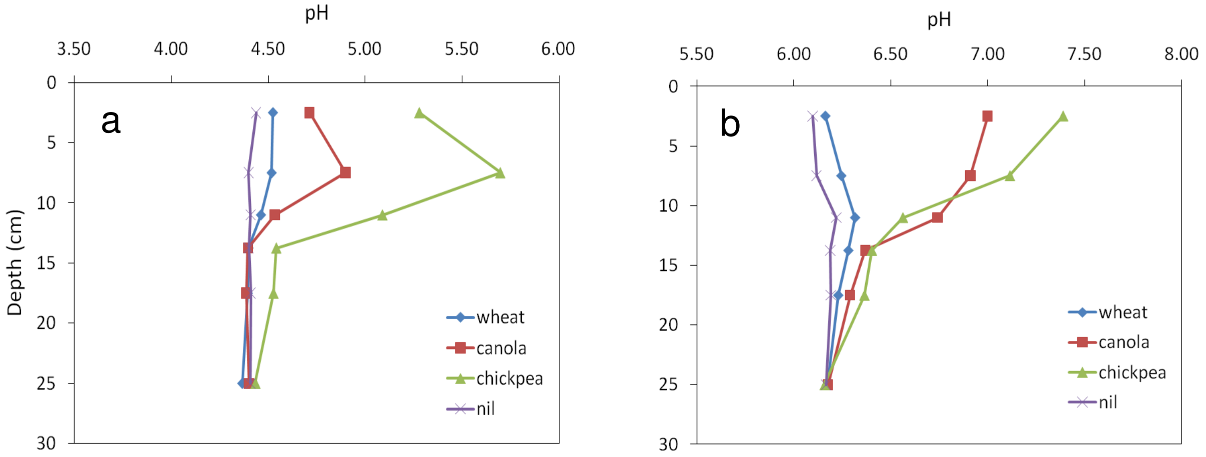

Figure 1. pH in (a) Frankston and (b) Shepparton soils at 2 months after the addition of canola, chickpea and wheat residues (Unpublished Data).

Experiment 2

This experiment confirmed that the soluble fractions of agricultural residues are important for pH change (Figure 2). This agrees with other studies which show that two-thirds of available alkalinity of a range of plant material is soluble (Sakala *et al*., 2004). This soluble fraction was the main source of alkalinity within the first 2 days. However, acidification occurred after 2 days in soil receiving the soluble fraction of chickpea most likely due to nitrification as the chickpea residue has a high N content (Table 1). The pH changes observed by whole residues were similar to those observed in the field study. While the potential alkalinity provided a suitable indicator to the relative liming potential of each residue, it was inadequate to predict the absolute pH change. For example, canola had more than 85% of the alkalinity of chickpea, but did not result in comparable change in pH (Figure 1). Further analyses of the chemical composition of the soluble fraction of each residue are required. In addition, quantifying changes in chemical composition of residues during decomposition would provide a useful link to studies which have examined the role of specific chemical functional groups using model compounds (Rukshana *et al*., 2009).

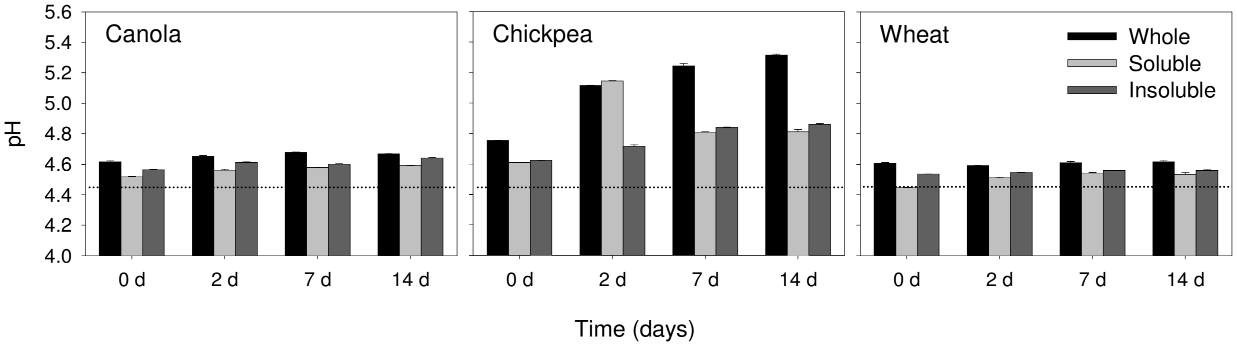

Figure 2. pH in Frankston soil after incubation with whole, soluble and insoluble components of canola, chickpea and wheat residues. Bars indicate standard error of the mean (n=3) and dotted lines the initial soil pH (Butterly *et al*., 2009a).

Conclusions

Soil pH changes after the addition of canola, chickpea and wheat were related to their alkalinity and N contents. The greatest increase in soil pH occurred after chickpea addition as it is easily mineralised (i.e. low C: N) and had the highest potential alkalinity than either canola or wheat. Ash alkalinity should be considered a coarse indicator of pH change, especially in the short-term since it was insufficient to predict the alkalinity contribution of canola. The soluble fraction contained a significant proportion of the total alkalinity for all residues. The soluble fraction was the main source of alkalinity within the first 2 days; however this fraction has the potential to acidify if it contains high concentrations or N. A better understanding of the biochemical process is required to accurately predict pH changes. Further studies should explore a wider range of agriculturally important residues and employ novel technologies to understand the interactions between residue chemistry and the soil environment.

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