

The contribution of crop residues to changes in soil pH under field conditions

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Abstract

Background and Aims Crop residues are important for the redistribution of alkalinity within soils. A net increase in pH following residue addition to soil is typically reported. However, effects are inconsistent in the field due to confounding soil processes and agronomic practises.

Methods A column experiment investigated the effects of canola, chickpea and wheat residues, differing in alkalinity content and C:N ratio, on soil pH changes in a Podosol (Podzol; initial pH 4.5) and Tenosol (Cambisol; initial pH 6.2) under field conditions.

Results Residues (10 g dry matter kg⁻¹ soil; 0–10 cm) increased soil pH, and temporal changes in alkalinity depended on the residue and soil type. Alkalinity was generated via abiotic association reactions between H⁺ and added organic matter and via ammonification and decarboxylation processes during decomposition.

Alkalinity from canola and chickpea residues moved down the soil profile (10–30 cm) and was attributed to nitrate immobilisation and organic anion decomposition by soil microbes.

Conclusions The application of residues to acid and moderately acid soils increased the pH of both topsoil and subsoils, which persisted over 26 months. Maximal increase of pH observed at 3 months was correlated with the concentration of excess cations in the residues.

Keywords Decomposition · Initial pH · Long-term · Nitrogen cycle · Soluble alkalinity · Soil acidification · Soil type

Introduction

The retention of crop residues is important for the redistribution of alkalinity within soils. A number of laboratory incubation studies have shown that plant material increases pH (Hoyt and Turner 1975; Ritchie and Dolling 1985; Bessho and Bell 1992; Pocknee and Sumner 1997; Tang et al. 1999). In general, pH changes are related to ash alkalinity and excess cations (Noble and Randall 1999; Tang et al. 1999), which indicate the concentration of organic anions within the materials. Increases in pH via the C cycle occur through H⁺ association with organic compounds and the decarboxylation of organic anions in the residue (Yan et al. 1996). Theoretically, H⁺ association will

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occur if the pKa of the acid groups of the organic compounds is greater than the soil pH (Ritchie and Dolling 1985). Through the N cycle, ammonification of organic N and nitrate uptake increase pH whereas nitrification and ammonium uptake decrease pH (Helyar and Porter 1989). However, the effect of residues on pH change varies widely between studies due to differences in residue composition and soils used. In particular, the initial pH of the soil is important for the pH change (Tang and Yu 1999).

Few studies have investigated the direct effect of residues on soil pH change in the field. The contribution of residues to changes in soil pH is often confounded by other components of the soil-plant system. A number of long-term field trials have observed soil acidification where residues have been retained (Conyers et al. 1996; Slattery et al. 1998; Paul et al. 2001; Xu et al. 2002), which was largely due to high soil N status. In fact, burning (Heenan and Taylor 1995) and removal (Xu et al. 2002) of stubble reduced acidification, indicating that the stubbles were enhancing mineralisation and N supply from other sources.

In most cases, residues would not be expected to cause net acidification. Poss et al. (1995) showed that alkalinity generated by wheat residues in the surface soil was simply alkalinity removed from the soil during plant growth. Nevertheless, residues with high N content (low C:N) are likely to cause acidification during later stages of decomposition. However, even for lucerne hay, Evans et al. (1998) showed that alkalinity generated was proportional to acidification caused by nitrification and nitrate leaching. It is inherently difficult to assess the direct biochemical effects of residues on soil pH from agronomic or management processes. Soil pH change by residues will depend on the relative contribution of alkalinity-producing or consuming processes and the depth at which they occur.

The experiment described here aimed to (a) quantify the change in soil pH associated with residues of canola, chickpea and wheat, (b) determine the contribution of C and N cycling process within two soil types, and (c) examine the effect of surface residue application on pH change in subsoil layers. To our knowledge this is the first investigation to quantify the temporal and spatial effects of these processes under field conditions. We hypothesised that (a) residues would increase pH and the magnitude of the increase would be related to alkalinity content and initial soil pH and (b) increases in pH would be transient in soils amended with residues with high nitrogen content (low C:N) due to nitrification and nitrate leaching.

Materials and methods

Soil and residue collection

Soil was collected from Frankston (38 °14'S, 145 ° 22'E) and Shepparton (36 °28'S, 145 °36'E), Victoria, Australia, air-dried, sieved (<2 mm) and thoroughly mixed as described in Butterly et al. (2011). These soils are classified as Podosol and Tenosol (Isbell 1996) or Podzol and Cambisol (FAO/ISRIC/ISSS 1998), respectively, and were chosen based on their initial pH and low buffer capacity. Briefly, the physicochemical properties of the Frankton soil were; pH 4.5, total C 2.9 g kg⁻¹, total N 0.11 g kg⁻¹, C:N 26.4, sand 97.3%, silt 1.1%, clay 1.6%. The corresponding properties of the Shepparton soil were; pH 6.2, total C 1.9 g kg⁻¹, total N 0.21 g kg⁻¹, C:N 9.0, sand 81%, silt 5.8%, clay 13.2%. Residues of canola (*Brassica napus* L.), chickpea (*Cicer arietinum* L.) and wheat (*Triticum aestivum* L.) were collected from field-grown crops after harvest, dried at 70 °C and finely ground (<2 mm). Chemical properties of the residues are outlined in Table 1.

Table 1 Chemical properties of crop residues used in the study (Data from Butterly et al. 2011)

Residue	Cations (g kg ⁻¹)				Anions (g kg ⁻¹)			Excess cations (cmol kg ⁻¹)	Total C (g kg ⁻¹)	Total N (g kg ⁻¹)	C:N	EOC (g kg ⁻¹)
	Ca	K	Mg	Na	Cl	P	S					
Canola	9.9	14.8	5.1	13.2	12.4	0.5	5.7	114	411	10.0	41	30
Chickpea	13.8	27.0	4.6	0.5	4.2	1.4	3.2	142	426	11.7	36.3	37
Wheat	2.5	13.3	1.7	0.4	1.8	0.6	1.9	43	439	5.8	76	46

Extractable organic C (EOC)

Experimental design and column construction

PVC columns (10 cm ID×35 cm high, IPLEX Pipelines, Australia) were longitudinally sectioned and rejoined with tape and silicone. Soil columns were constructed by firstly filling the lower section (10–30 cm) with air-dry soil. A small number of plastic beads were placed around the edge of the column on the top of this layer to ensure that the residue interface could be relocated at each sampling. For each 0–10 cm layer, soil was thoroughly mixed with respective residues at 10 g dry matter kg⁻¹ soil (14 t ha⁻¹) before being transferred to the top of each column. The bulk densities of soil within the columns were 1.45 g cm⁻³ for the Podosol and 1.24 g cm⁻³ for the Tenosol. The columns were then wet to 60% field capacity and allowed to stand overnight. On the following day the columns were inverted and resin traps were fitted at the base using silicone. Based on the design of Anderson et al. (1998), each resin trap consisted of 110 g (wet weight) of 1:1 mix of Amberlite IRA458 Cl⁻ anion exchange resin and Amberlite 1200 H⁺ cation exchange resin (Rohm Haas Company, Philadelphia, PA, USA) held within the plastic frame (10 cm OD×2.5 cm high) with fine nylon mesh (3.5 μm, Sefar Pty Ltd, Australia). Overall, the experiment consisted of a full factorial design with 2 soils×4 residue treatments×3 replicates×5 sampling times.

Field site

Soil columns were placed in the field from August 2008 to October 2010 on the University farm (37°72'S, 145°05'E). Columns were randomly arranged within

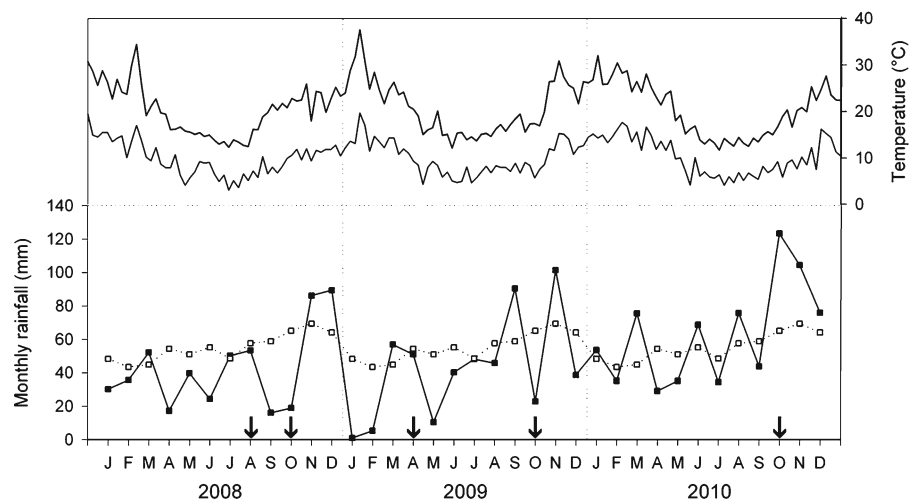
trenches, and backfilled with clean white sand to ensure that resin traps were not contaminated by the surrounding soil. The site had a gradual slope to ensure trenches were free draining. The columns and surrounding area were kept weed free in order to limit contamination from foreign plant material. Meteorological information for 2008 to 2010 is shown in Fig. 1.

Sampling

Columns were sampled at 0, 3, 9, 15 and 26 months that occurred on the 12th Aug 2008, 13th Oct 2008, 22nd April 2009, 12th Oct 2009 and 13th Oct 2010, respectively. The first sampling time (0 month) was performed the following morning (~18 h) after the columns were constructed and prior to installing the remaining columns in the field. At each time the columns remaining in the field were fitted with new resin traps and randomly allocated within the trenches as before.

At each sampling time, a set of 24 columns were removed from the field and destructively sampled. Resin traps were removed and each column was sectioned into depths of 0–5, 5–10, 10–12, 12–15, 15–20 and 20–30 cm. Smaller depth increments were used below the amended layer for increased precision. Samples were transferred to individual plastic bags, thoroughly mixed and stored at 4 °C overnight. The gravimetric water content of soil was determined after drying a subsample at 105 °C for 24 h. On the second day, soil nitrogen (N) was determined on field moist soil as described below, and the remaining sample was dried at 25 °C for other analyses. The contents of the resin traps were removed and stored at 4 °C.

Fig. 1 Minimum and maximum weekly mean temperatures, monthly rainfall (■) during 2008–2010 and the 32-year monthly mean rainfall (□) at Bundoora, Victoria. Arrows indicate sampling times



Physicochemical analyses

Soil texture was characterised by determining the particle-size distribution using a Laser Particle Size Analyser (Malvern Mastersizer 2000, Worcestershire, UK). The gravimetric water content at field capacity was determined using the hanging column-constant head burette technique (Reynolds and Clarke Topp 2007). Total C and N contents of soils and residues were quantified using an Elementar Vario EL analyser (Elementar Analysensysteme GmbH, Hanau, Germany). Extractable organic C (EOC) content of the residues was determined following water (1:10 w/v) extraction at 70 °C according to Butterly et al. (2011). Concentrations of total Ca, Mg, P and S within plant residues were determined using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) (GBC Scientific, Melbourne, Australia), and K and Na using a Sherwood 420 Flame Photometer (Sherwood Scientific, Cambridge, England) following digestion with nitric:perchloric acids (4:1). For Cl^- determination, 1 g of residue was extracted with 10 ml hot water (70 °C) for 1 h, supernatants were passed through 0.45 μm membrane filters and the Cl^- concentration was quantified using a Metrohm 883 Plus ion chromatograph (Metrohm, Herisau, Switzerland). The excess cation content of the residues, calculated as the difference in charge concentration between cations (Ca^{2+} , Mg^{2+} , K^+ and Na^+) and anions (SO_4^{2-} , Cl^- and H_2PO_4^-) (Tang and Yu 1999) was used to estimate the alkalinity content. All analyses were performed in duplicate.

Soil N was extracted on field moist soil using 25 g soil (dry weight) with 2 M KCl (1:1) by shaking end-over-end for 1 h, centrifuging at 2000g for 5 min and filtering through Whatman 1 filter papers (Whatman International, Maidstone, England). Filtered extracts were frozen and later analysed for nitrate+nitrite ($\text{NO}_3^- + \text{NO}_2^-$) and ammonium (NH_4^+) using a QuickChem 8500 Flow Injection Analyser (Lachat Instruments, Loveland, CO, USA). Soil pH was determined on air-dried soil by extracting 5 g soil with 0.01 M CaCl_2 (1:5) using an end-over-end shaker for 1 h followed by centrifuging at 492g for 10 min. The pH of the supernatant was determined using a Thermo Orion pH meter (Thermo Orion 720A+, Beverly, MA, USA).

For the resin traps, N was extracted as described for soil, using 25 g resin but omitting the centrifugation step. For cation and anions, the same extraction procedure was used as for soils but using 1 M HCl instead

of 2 M KCl. Concentrations of Ca, Mg, P and S within HCl extracts were determined using ICP-OES, and K and Na using a Flame Photometer as previously described.

Net alkalinity production

pH buffer curves were established from pH 4 to 6.5 for the Podosol, and 5 to 7 for the Tenosol, by shaking soil in 0.01 M CaCl_2 (1:5) with varying amounts of HCl or K_2CO_3 . In the same way, pH buffer capacity (pHBC) of the surface soils (0–5 cm) was determined by adding 0.1 $\text{cmol H}^+/\text{OH}^- \text{ kg}^{-1}$ soil, to quantify temporal changes in pHBC following residue amendment. The net change in alkalinity ($\text{cmol OH}^- \text{ kg}^{-1}$ soil) for each treatment was estimated from the difference in pH between residue-amended and non-amended treatments using the inverse slope of the appropriate pHBC for each soil, depth and incubation time. Net alkalinity production was calculated for each individual column ($\text{cmol OH}^- \text{ column}^{-1}$) using the net change in alkalinity ($\text{cmol OH}^- \text{ kg}^{-1}$ soil) of each depth and the mass of soil in each layer.

Statistical analyses

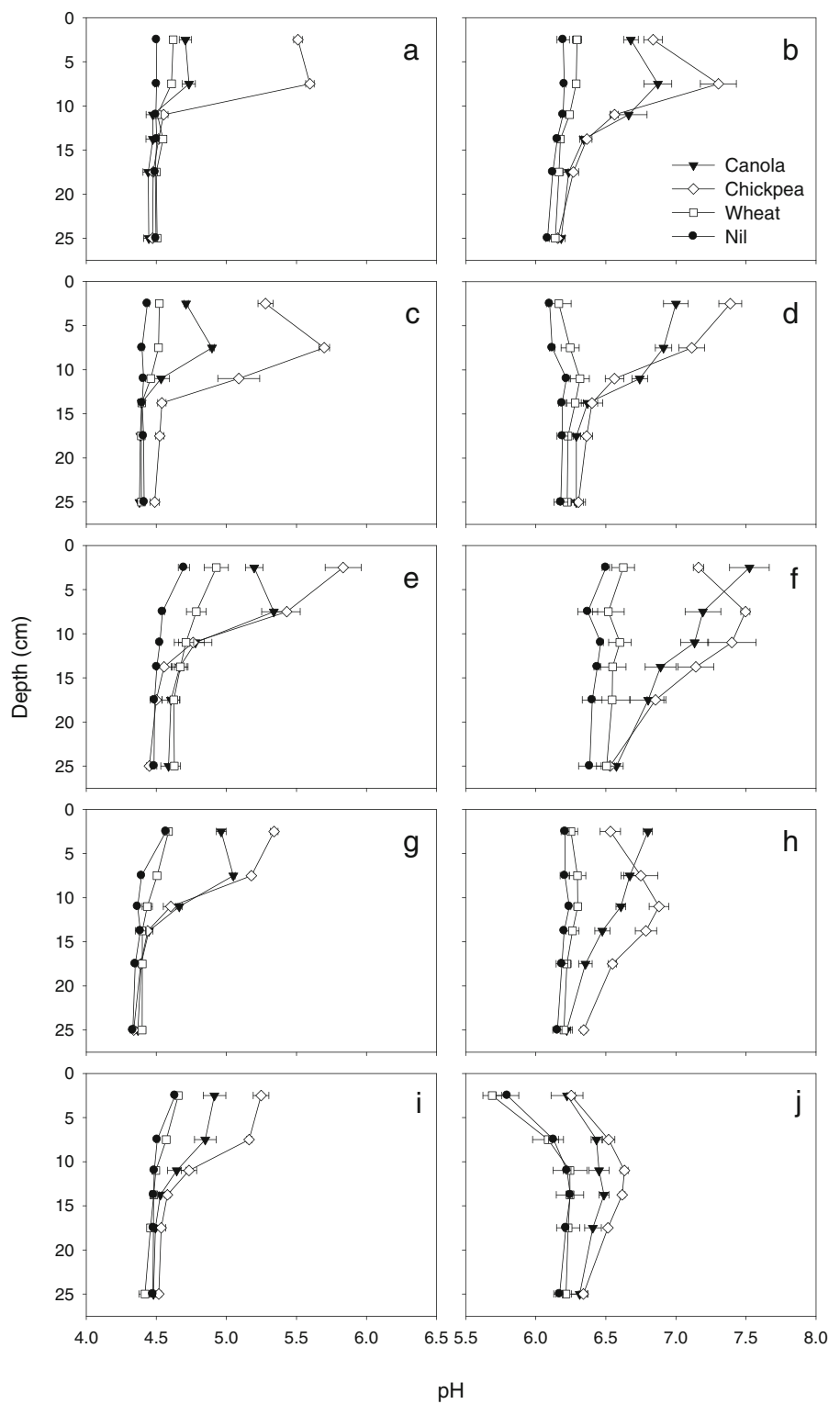
For each sampling time, a two-way repeated measures analysis of variance (rmANOVA) in a completely randomised designed was performed using Genstat 10th Edition (VSN International, Hemel Hempstead, England) to test the treatment effects on soil pH, and concentrations of $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ using soil and residue type as main factors and sampling depth as the repeated measure. For Ca, K, Mg, Na, NH_4 , $\text{NO}_3 + \text{NO}_2$, P and S concentrations in resin traps and net alkalinity production, a two-way ANOVA was performed using soil and residue as the main factors. For all significant ($P \leq 0.05$) main effects and their interactions a Least Significant Difference (LSD) test was used to identify significant ($P = 0.05$) differences between means.

Results

Soil pH

Amendment of surface (0–10 cm) layers with residues immediately (0 month; 18 h) increased soil pH in both soils with the increase being largest for chickpea and smallest for wheat-amended soils (Fig. 2). While pH

Fig. 2 Soil pH in Podosol (left; a, c, e, g, i) and Tenosol (right; b, d, f, h, j) soils at 0 (a, b), 3 (c, d), 9 (e, f), 15 (g, h) and 26 (i, j) months either amended (0–10 cm) with canola, chickpea and wheat residues or non-amended control (nil). Bars indicated standard error of the mean ($n=3$)



increases in the Podosol were confined to the amended layer, the pH in the Tenosol was also increased in the

10–15 cm layers. Since the columns were destructively sampled within 24 h after construction, the results

indicated some leaching of alkalinity from the amended layer in the Tenosol when the water content was adjusted to 60% field capacity.

Further increases in pH of the amended soil layers occurred over time and depended on the residue and soil type (Fig. 2). Generally, the magnitude of the pH change was related to the excess cation concentration of the materials (Table 1). Chickpea amendment resulted in the largest pH changes in both soils, with the maximum increase of approximately 1.3 units occurring in Podosol and Tenosol at 3 months. In comparison, canola amendment increased pH by 0.82 and 1.02 units in Podosol and Tenosol, respectively with the maximum occurring at 9 months. Further, the change in pH of canola-amended Tenosol was much less than that for the Podosol after 3 and 9 months, and thereafter soil pH generally decreased in the surface layers until the end of the study.

Residue addition increased the pH of the non-amended subsoil layers over time with the increase being greater in the Tenosol than the Podosol (Fig. 2). In the Podosol, the increase mainly occurred in the 10–12 cm layer following chickpea amendment, whereas in the Tenosol the pH increase occurred in 10–30 cm layers in order of chickpea>canola>wheat residue.

Surface soils (0–5 cm) of the Tenosol had acidified more than expected by the final sampling time and occurred irrespective of treatment (Fig. 2j). The presence of an unidentified *Bryophyte* on the surface of the columns was apparent during 2010 and this could have been the cause of this observation. This acidification was not observed in the Podosol.

Soil nitrogen

The concentrations of $\text{NO}_3^- + \text{NO}_2^-$ (NO_x) and NH_4^+ were low in the non-amended Podosol and Tenosol (nil) during the study (Figs. 3 and 4). Residue addition immediately increased NH_4^+ concentration ($P < 0.05$) (0 month) with the increase being greater in the Tenosol than the Podosol (Fig. 3). The largest increases were 12 mg kg^{-1} and 7.5 mg kg^{-1} in the Tenosol amended with chickpea and canola, respectively. Addition of wheat residue only increased NH_4^+ concentration by up to 1 mg kg^{-1} . The temporal change in net NH_4^+ concentration differed between the soils. While the greatest change in NH_4^+ concentration occurred immediately (0 month) in the Tenosol,

this was delayed in the Podosol (3 months). During subsequent incubation (9–26 months) NH_4^+ concentration remained low ($\leq 3 \text{ mg N kg}^{-1}$) in all treatments.

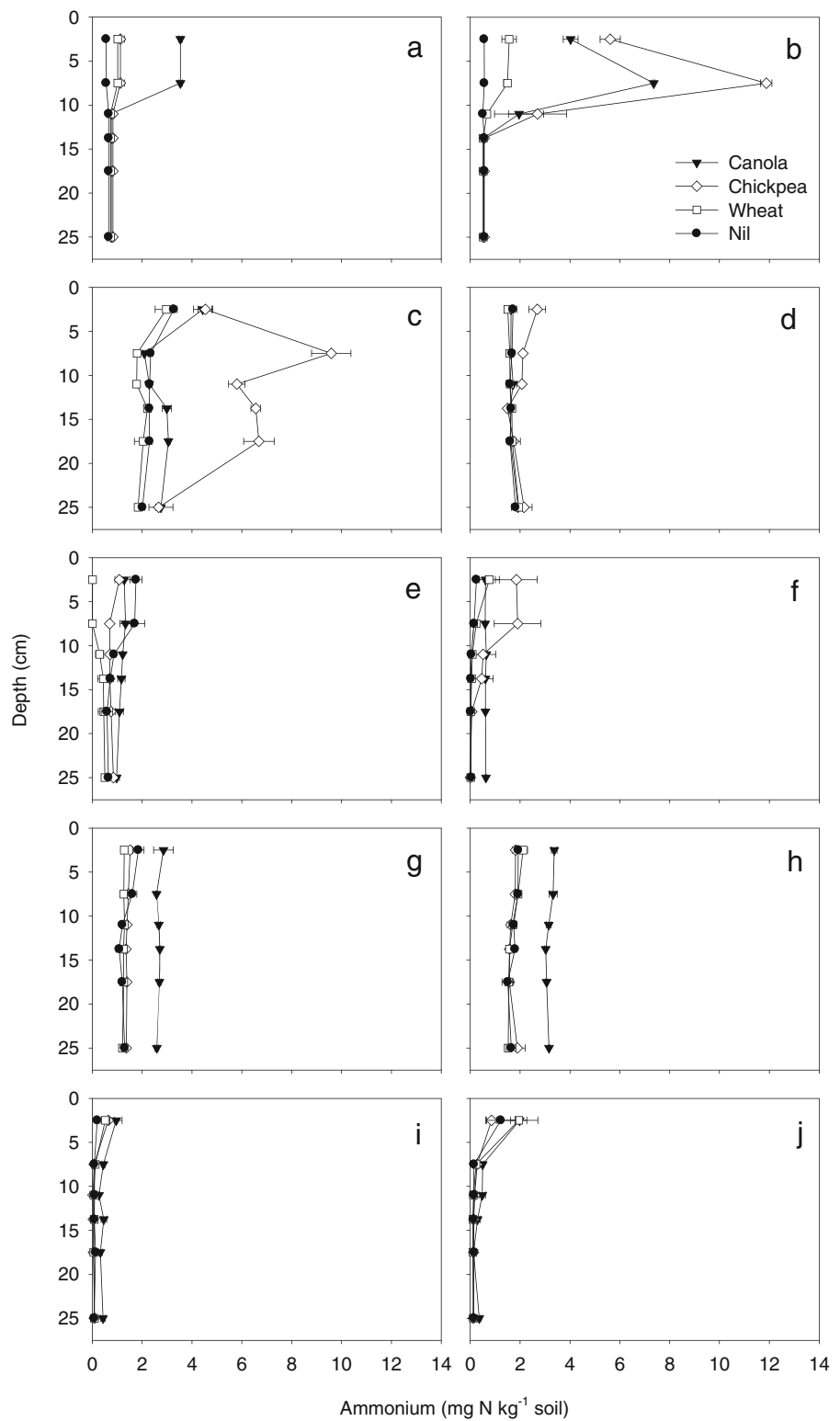
Canola amendment immediately (0 month) increased NO_x concentration, up to 20 and 45 mg kg^{-1} in the Podosol and Tenosol, respectively (Fig. 4). Chickpea and wheat residues only increased NO_x concentration by 3 and 12 mg kg^{-1} , respectively in the Tenosol and had no effect in the Podosol. In general, no further increase in NO_x concentration occurred in the Podosol during subsequent incubation. In contrast, a net increase in NO_x concentration was observed at 3 and 9 months in the Tenosol amended with chickpea. Over the 26-month incubation period, downward movement of NO_x occurred from the amended layer and was mostly pronounced in the chickpea-amended Tenosol (Fig. 4h). By 26 months, NO_x concentration was negligible in all other treatments except the canola-amended Tenosol.

Anions and cations in resin traps

Concentrations of anions and cations in the resin traps are presented in Table 2. A significant ($P \leq 0.05$) effect of residue amendment on Ca concentration was observed in the canola-amended Tenosol at 9 months (Table 2). The amount of Ca leached at 9 and 15 months was greater in the Podosol ($2.3\text{--}3.1 \text{ mg Ca column}^{-1}$) than in the Tenosol ($2 \text{ mg Ca column}^{-1}$), respectively. For K, only the chickpea-amended Podosol had higher K concentration than the control at 15 months ($P \leq 0.05$). The Mg concentration only differed between treatments at 9 months with increases of 1.2 and $2.4 \text{ mg Mg column}^{-1}$ in the Podosol and Tenosol following chickpea and canola amendment, respectively. Compared to controls, Na concentration increased in the Podosol amended with canola at 15 and 26 months, and with chickpea residue at 26 months but decreased in wheat-amended Podosol at 26 months. Residue addition did not affect NH_4^+ concentration in the resin traps in either soil, except an increase of $2.9 \text{ mg NH}_4^+ \text{ column}^{-1}$ at 9 months in the chickpea-amended Podosol.

Addition of canola and chickpea residues generally increased the concentration of NO_x from 9 months, with the concentration being greater in the Tenosol than the Podosol at 9 and 26 months (Table 2). These results correspond with the downward movement of NO_x through the soil profile (Fig. 4). Although the concentration of P in resin traps was

Fig. 3 Ammonium concentration in Podosol (*left*; **a, c, e, g, i**) and Tenosol (*right*; **b, d, f, h, j**) soils at 0 (**a, b**), 3 (**c, d**), 9 (**e, f**), 15 (**g, h**) and 26 (**i, j**) months either amended (0–10 cm) with canola, chickpea and wheat residues or non-amended control (nil). Bars indicate standard error of the mean ($n=3$)



generally low, addition of canola and wheat residues increased it in the Podosol (Table 2). Concentrations

of S were highly variable and were probably due to the use of H₂SO₄ during the commercial preparation of

Fig. 4 Nitrate concentration in Podosol (*left*; **a, c, e, g, i**) and Tenosol (*right*; **b, d, f, h, j**) soils at 0 (**a, b**), 3 (**c, d**), 9 (**e, f**), 15 (**g, h**) and 26 (**i, j**) months either amended (0–10 cm) with canola, chickpea and wheat residues or non-amended control (nil). Bars indicate standard error of the mean ($n=3$)

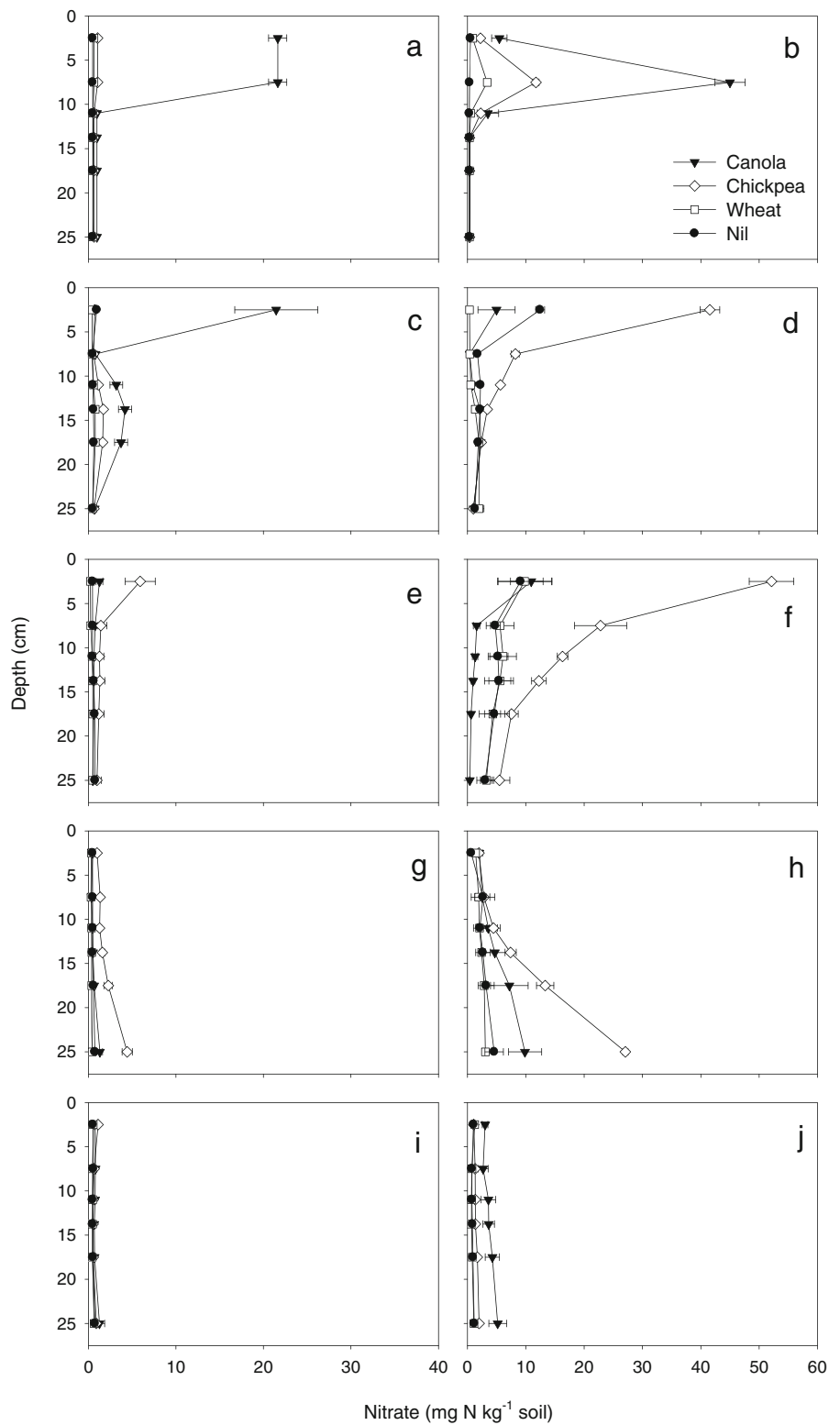


Table 2 Amounts of anions and cations (mg column⁻¹) in resin traps of Podosol and Tenosol soils either amended with canola, chickpea and wheat residues or non-amended control (Nil) during various experimental periods

Ion	Time (months)	Podosol				Tenosol				LSD <i>P</i> >0.05	Significance level		
		Canola	Chickpea	Wheat	Nil	Canola	Chickpea	Wheat	Nil		Soil (S)	Residue (R)	S×R
Ca	3	1.7	2.0	2.1	1.6	2.5	1.9	1.7	2.3	-	n.s.	n.s.	n.s.
	9	1.9	1.6	1.5	1.6	5.3	3.7	3.3	3.3	0.9	**	**	*
	15	3.2	4.9	4.1	1.8	8.1	8.0	4.3	4.8	2.0	**	n.s.	n.s.
	26	19.5	12.4	9.3	13.7	16.5	14.0	15.6	10.0	-	n.s.	n.s.	n.s.
K	3	5.7	9.1	6.5	7.7	7.5	5.1	5.3	5.3	-	n.s.	n.s.	n.s.
	9	11.9	15.7	10.8	13.2	17.9	15.1	13.9	11.1	-	n.s.	n.s.	n.s.
	15	10.6	23.9	9.9	6.7	23.8	17.9	12.1	11.7	7.9	n.s.	***	*
Mg	3	33.5	35.5	23.3	26.5	42.4	28.2	41.2	24.8	-	n.s.	n.s.	n.s.
	9	4.2	4.2	4.3	3.7	4.2	3.8	3.8	3.6	-	n.s.	n.s.	n.s.
	15	3.6	5.1	3.2	3.9	5.3	3.0	2.6	2.9	1.2	n.s.	**	***
	26	4.9	6.0	4.9	3.0	6.3	5.9	3.4	3.8	-	n.s.	n.s.	n.s.
Na	3	17.7	11.1	10.1	17.8	13.5	11.5	11.6	7.9	-	n.s.	n.s.	n.s.
	9	41.5	46.0	39.0	47.5	43.5	35.5	34.5	37.3	-	n.s.	n.s.	n.s.
	15	50.1	52.6	45.4	52.2	40.8	28.8	22.3	28.3	6.7	***	*	n.s.
	26	51.3	42.9	37.1	28.4	45.0	32.8	30.3	23.0	12.5	n.s.	**	n.s.
P	3	64.7	54.9	22.6	46.1	50.5	49.0	45.7	59.4	7.3	**	***	n.s.
	9	0.08	0.08	0.10	0.09	0.15	0.14	0.15	0.10	0.02	***	n.s.	n.s.
	15	0.24	0.21	0.15	0.11	0.14	0.35	0.32	0.37	0.17	*	n.s.	*
	26	0.13	0.14	0.22	0.17	0.19	0.40	0.29	0.29	0.10	*	n.s.	n.s.
S	3	1.76	0.45	1.18	0.47	0.70	0.53	0.69	0.63	0.45	*	***	**
	9	124	128	119	115	104	147	93	132	-	n.s.	n.s.	n.s.
	15	80	79	81	76	90	83	86	78	4.79	*	n.s.	n.s.
	26	80	73	72	58	74	108	66	103	-	n.s.	n.s.	n.s.
NH ₄	3	46	114	46	158	134	121	128	108	53.7	*	n.s.	**
	9	1.8	1.6	1.6	1.5	2.0	2.0	1.5	2.1	0.23	n.s.	*	n.s.
	15	4.2	6.3	3.4	3.9	2.7	2.4	2.1	2.8	0.87	***	***	***
	26	2.3	2.0	2.3	2.0	2.4	2.8	2.0	1.8	-	n.s.	n.s.	n.s.
NO ₃	3	3.4	3.3	2.6	3.3	5.0	3.5	3.7	3.4	0.69	*	n.s.	n.s.
	9	4.8	4.1	4.2	4.1	5.3	5.4	4.0	5.8	-	n.s.	n.s.	n.s.
	15	18.7	14.4	10.9	12.3	26.5	20.8	14.1	21.5	3.9	***	***	n.s.
NO ₂	3	32.4	30.3	23.0	17.9	52.0	73.8	30.1	30.1	14.9	n.s.	**	n.s.
	26	70.5	67.7	57.1	52.9	141.7	76.8	65.9	58.7	24.7	***	***	**

***, **, * and n.s. represent $P < 0.001$, $P < 0.01$, $P < 0.05$, $P > 0.05$, respectively.

the resin. However, the data do not indicate any additional leaching loss of S under any residue treatments.

Net alkalinity production

Significant interactions between soil and residue occurred on pH buffer capacity (pHBC) of the topsoil

(Table 3). While addition of canola and chickpea increased the pHBC only in the Tenosol at 3, 15 and 26 months, wheat residue tend to decrease it in the Podosol at 3 months.

In general, net alkalinity production was related to the amount of alkalinity added as residues with chickpea residue being greatest and wheat being smallest

Table 3 pH buffer capacity (pHBC) ($\text{cmol pH}^{-1} \text{kg}^{-1}$) of Podosol and Tenosol topsoils (0–5 cm) either amended with canola, chickpea and wheat residues or non-amended control (Nil)

Time (months)	Podosol				Tenosol				LSD $P=0.05$	Significance level		
	Canola	Chickpea	Wheat	Nil	Canola	Chickpea	Wheat	Nil		Soil (S)	Residue (R)	S×R
3	0.56	0.51	0.45	0.60	0.95	1.14	0.49	0.36	0.281	**	**	**
9	0.42	0.36	0.42	0.49	0.55	0.44	0.50	0.36	-	n.s.	n.s.	n.s.
15	0.37	0.44	0.42	0.43	0.51	0.48	0.44	0.30	0.077	n.s.	**	***
26	0.39	0.38	0.43	0.41	0.38	0.35	0.30	0.30	0.048	***	n.s.	**

***, **, and n.s. represent $P < 0.001$, $P < 0.01$, $P > 0.05$, respectively

(Fig. 5). Addition of residues immediately (0 month) increased the alkalinity production, and the alkalinity production peaked at 3 months for chickpea residue in both soils and canola in the Podosol, and 9 months for the other treatments. The net alkalinity production

occurred in canola- and chickpea-amended soils until the end of the study. The immediate (0 month) net alkalinity production following chickpea residue addition to Podosol and Tenosol represented the release of 36 and 24% of the total alkalinity, respectively. In the Tenosol, canola and chickpea released 78 and 89% of their total alkalinity content at 3 months, respectively. In the Podosol, chickpea released only 50% of its total alkalinity content after 3 months, while canola released only 39% after 9 months.

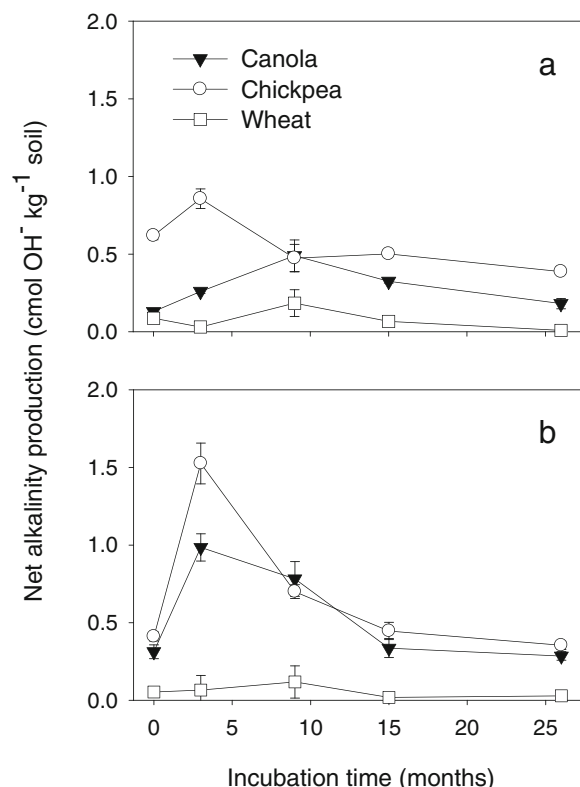


Fig. 5 Net alkalinity production ($\text{cmol OH}^{-1} \text{column}^{-1}$) in Podosol (a) and Tenosol (b) soils amended with either canola, chickpea or wheat residue. Bars indicate standard error of the mean ($n=3$). The amounts of alkalinity added as canola, chickpea and wheat residues were 1.26, 1.72 and 0.52 $\text{cmol OH}^{-1} \text{column}^{-1}$ soil, respectively

Discussion

Effect of residue type on soil pH change

This study showed that soil pH immediately (0 month; 18 h) increased following the incorporation of crop residues and that changes in alkalinity over time depended on the residue type (Figs. 1 and 5). The immediate increase in pH of the residue-amended layer was attributed to abiotic association reactions between H^{+} ions and organic anions (Hoyt and Turner 1975; Tang and Yu 1999; Rukshana et al. 2011), biological decarboxylation of organic anions (Yan et al. 1996) and the ammonification of organic N compounds (Helyar and Porter 1989). Net alkalinity generation was the greatest for canola and chickpea, and maximal values generally occurred at 3 months (Fig. 5). In a laboratory incubation study using the same soils and residues, we observed that alkalinity was released within 14 days (Butterly et al. 2011). Therefore, it is likely that the actual generation of alkalinity could have occurred early within the first 3-month period and is likely to be dominated by biological decarboxylation and N cycle processes.

The maximal alkalinity generated was proportional to the added alkalinity and the amount of organic N available to undergo ammonification (Fig. 6) (Table 1). The relationship between alkalinity production and alkalinity content, as indicated by the concentrations of excess cations, has been well established (Noble et al. 1996; Tang et al. 1999). While complete decomposition of residues is not necessary for substantial changes in pH to occur (Tang et al. 1999), it has been suggested that no more than one third of the pH change is due to non-biological mechanisms (Tang and Yu 1999). In contrast, wheat residue did not generate any further alkalinity during the 26-month study and may indicate that the initial pH increase occurred independent of decomposition. Other studies have observed that acid soils (pH 4.1–4.6) amended with wheat residue increased to maximal pH quickly and remained constant (Xu and Coventry 2003), and in fact can remain stable for long periods (8 to 574 days) (Pocknee and Sumner 1997). Further, altering the frequency at which wheat residue was added, had no effect on proton consumption and thus pH change (Duong et al. 2009). In the current study, only 35 and 23% of the alkalinity added ($0.52 \text{ cmol kg}^{-1}$ soil) as wheat residue was released in the Podosol and Tenosol, respectively.

After the maximal alkalinity production was reached, net acidification of the soil layer amended with canola and chickpea occurred until the end of the experiment. Nitrification and subsequent nitrate leaching was primarily responsible for the pH decline which is consistent with other studies (Xu and Coventry 2003; Xu et al. 2006). During the mineralisation of organic N, the net effect of ammonification (-1 mol H^+) and nitrification

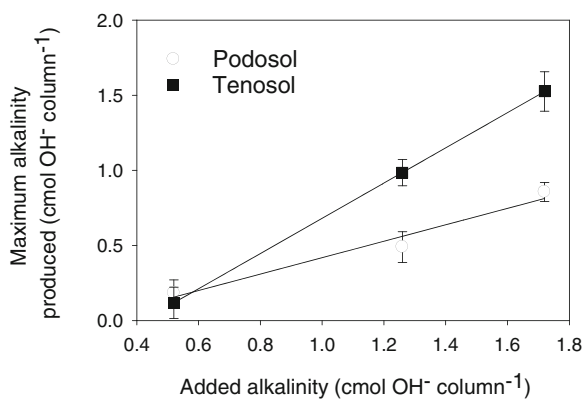


Fig. 6 The relationship between added alkalinity and maximum net alkalinity production ($\text{cmol OH}^- \text{ column}^{-1}$) in Podosol and Tenosol soils. Bars indicate standard error of the mean ($n=3$)

($+2 \text{ mol H}^+$) is acidification (Helyar and Porter 1989). Significant loss of nitrate from the soil layer amended with canola and chickpea was evident (Fig. 4). Despite the temporal differences in alkalinity generation between the residues, a net increase in alkalinity was observed for all residue treatments at the end of the experiment. Alkalinity not released by the end of the study is likely to be associated with less degradable or structural compounds of the residue.

Impact of soil type on soil pH change upon residue addition

Soil type affected both the amount of alkalinity generated following residue amendment and the changes in alkalinity over time (Figs. 1 and 5). The immediate (0 month; 18 h) increase in alkalinity following chickpea amendment was greater in the Podosol than the Tenosol (Fig. 5). Tang and Yu (1999) showed that alkalinity generation was greater in low initial pH soils than moderately acidic soils due to greater association reactions of H^+ with added residues. The association of H^+ with organic compounds occurs when the soil pH is less than the pK_a of the acid groups of the compounds (Ritchie and Dolling 1985). During this initial period, association reactions with organic anions are likely to be equally important for alkalinity generation as their decomposition, especially in the Podosol. The contribution of net ammonification to alkalinity generation would have been negligible in the Podosol, since ammonium concentrations were low (0 month; 18 h) and less than previously determined at 4 h after residue addition (Butterly et al. 2011).

The relative differences in maximum alkalinity production between soils are likely to reflect the proportion of the residue that was decomposed. A number of studies have shown that C and N mineralisation in residue-treated soils is highly pH dependant (Fu et al. 1987; Marschner and Kalbitz 2003; Kemmitt et al. 2006; Bertrand et al. 2007). Reductions in mineralisation at low pH can be due to low activity and survival of soil microbes and also to lower solubility of dissolved organic matter. In the current study 89% of the alkalinity of chickpea was released at 3 months in the Tenosol while only 50% was released in the Podosol. For canola, low initial pH reduced the amount of alkalinity generated and delayed the time to maximal alkalinity production (6 months) (Fig. 5). We have previously shown that decomposition of chickpea and canola was reduced in

the Podosol (Butterly et al. 2011). In fact, no significant change in pH occurred during incubation of canola-amended Podosol in the absence of leaching (Butterly et al. 2011). The high concentrations of ammonium in chickpea-amended Podosol at 3 months indicate that substantial ammonification had occurred and this process contributed to alkalinity generation in both soils.

The greater decline following the maximum alkalinity production in the Tenosol than the Podosol (Fig. 5) partly resulted from greater nitrification (increases in nitrate concentration) in the Tenosol between 3 and 15 months. Nitrification is generally more sensitive to low pH than ammonification (Robson and Abbott 1989). Further, net nitrification in the canola-amended Podosol was expected to be low since most of the initial pool of nitrate (Fig. 4a) was likely to be soluble inorganic N present within canola residue (Butterly et al. 2011). Our results indicate greater net alkalinity generation by chickpea in the Podosol than the Tenosol at the end of the study, despite a smaller change in maximal alkalinity. This is consistent with Tang et al. (1999) who showed that alkalinity generation was greater in low initial pH soils due to reduced nitrification in comparison with moderately acidic soils.

Vertical variation in soil pH change after residue addition

This study clearly demonstrated that amendment of surface soil layers (0–10 cm) affected increases in alkalinity deeper within the soil profile (10–30 cm) (Fig. 2). These increases in alkalinity in deeper soil layers could mainly result from movement and decomposition of the soluble component of the residues. A number of studies showed that a high proportion of the alkalinity within plant material is in the soluble fraction (Yan and Schubert 2000; Franchini et al. 2001; Sakala et al. 2004; Butterly et al. 2011). In a closed system, the mechanisms whereby net alkalinity is generated by soluble fractions via decarboxylation of organic anions as discussed earlier. Butterly et al. (2011) showed that net alkalinity generated by soluble residue fractions peaked by 14 days but was transient for residues with high N concentrations.

Leaching and transformation of N from the amended topsoil and/or N-containing compounds in the soluble fraction could also contribute to pH change in the subsoil layers. The current study demonstrated using free-draining columns that in an open system the

spatial separation of N mineralization and nitrification processes can occur via leaching. In the chickpea-amended Podosol, ammonium concentration was high below the amended soil layer at 3 months (Fig. 3c). Ammonium is generally considered to be less mobile in soil (Tang et al. 2000) although ~ 3 mg NH_4^+ was present in the resin trap of this treatment at 9 months (Table 2). Therefore, ammonium found below 10 cm could have originated from N mineralised in the amended layer or the mineralisation of soluble organic N deeper within the soil profile. Mineralisation and subsequent leaching of ammonium resulted in net alkalination of that layer. This process could have contributed to alkalinity generation in 10–20 cm of the chickpea-amended Podosol at 3 months (Fig. 2c).

Changes in nitrate concentration were greater than ammonium. Net nitrification occurred in canola and chickpea amended soils after 3 months. Nitrification is an acidifying process (Helyar and Porter 1989) and the leaching of nitrate with basic cations away from the soil layer where it is produced generates acidity (Bolan et al. 1991; Poss et al. 1995). Nitrate is known to be highly mobile in soils (Anderson et al. 1998). Since net alkalinity production, not acidification, occurred in the 10–20 cm layer, nitrate production must have been occurring in the amended layer in this study. Subsequent immobilisation of nitrate by soil microbes further down the soil profile is likely to contribute to alkalization below 10 cm. However, the extent of the contribution is unknown but is expected to be minor.

The C cycle would have also contributed to the generation of alkalinity below the amended soil layer. Similar to nitrate, dissolved organic matter and in particular organic anions can move down the soil profile associated with inorganic basic cations (Marschner and Noble 2000). In contrast, the association and mineralisation of the organic anions deeper within the soil profile would consume H^+ ions, release basic cations and result in an increase in base saturation. While the movement and release of base cations has been suggested as a mechanism of alkalinity generation (Williams 1980; Pocknee and Sumner 1997; Marschner and Noble 2000), direct evidence of this does not exist. We observed greater leaching of cations (Ca, K, Mg and Na) in residue-amended treatments than the non-amended controls (Table 2), and a strong correlation ($R^2=0.72$) between the charge concentrations (mol_c) of cations $\Sigma(\text{Ca}^{2+}+\text{K}^++\text{Mg}^{2+}+\text{Na}^+)$ and nitrate in the resin traps. The finding is consistent with Di and Cameron (2004),

suggesting that organic anions and nitrate are associated with cations and not H^+ ions during leaching. The limited effect of residues below the amended layer in the Podosol reflects the greater degree of acidity in this soil and the slower decomposition and release of alkalinity (Butterly et al. 2011; Rukshana et al. 2012).

Conclusions

This study demonstrated under field conditions that crop residues increased soil pH and temporal changes in alkalinity depended on residue and soil type. Maximum alkalinity released at 3 months was related to the alkalinity content of the residues and was reduced at low initial pH. Net acidification of soils amended with high N content residues occurred between 3 and 26 months. However, a net increase in alkalinity remained at the end of the 26-month study. This highlights that N-cycle acidification did not exceed alkalinity production, even for residues with high N content (low C:N). Overall, net alkalinity production was similar between soils despite large changes in magnitude during the study. Using free-draining columns we showed that residues incorporated into the soil surface generated alkalinity below the amended layer. Further, in the absence of external acidifying processes, alkalinity generated deeper within the soil profile persisted in a mildly acidic soil with a low pHBC. It appears that the soluble component of the residues had moved through the soil profile and contributed to the alkalization in subsoil layers. This has an important implication in minimizing subsoil acidification in dryland farming systems.

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