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Chemical and biological processes leading to the neutralisation of acidity in soil incubated with litter materials

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Abstract

Plant materials containing high amounts of ash alkalinity can be utilized to increase the pH of acid soils but the chemical and biological processes involved in the release of this alkalinity are not fully understood. In this laboratory study fresh leaf litter from two tree species (*Melia azedarach, Castanea sativa*) and sugarcane (*Saccharum officinarum*) trash containing ash alkalinities of 288, 141 and 33 $mmol_c\ kg^{-1}$ respectively, were mixed at three different rates (4, 16, 32 mg g^{-1}) with acidic topsoil from a Ultic Palexeralf and incubated at 90% WHC and at 25°C for 20 d while monitoring CO_2-evolution. Treatment effects were assessed by measuring changes in pH, acid buffering curves and exchangeable cations before and after incubation. Furthermore, soluble organic compounds, mineral N-forms were determined in soil extracts. Immediately after mixing, up to 50% of the added alkalinity was available for acid neutralisation. After incubation, acid neutralisation capacity at pH 4 (ANC_{pH4}) and the pH of the soils with the two higher amendment rates had increased in all treatments. The changes were most pronounced in the *Melia* amended soils, followed by *Castanea* and sugarcane and reflected the added amounts of ash alkalinity. In all treatments, soil respiration increased with amendment rate and was closely related to a decline in soluble organic carbon during incubation. Together with the shift from stronger to weaker acidity observed after incubation, this is evidence for the microbial decarboxylation of soluble organic anions.

Keywords: Acid neutralisation; Mineralization; Ash alkalinity; Litter; DOC

1. Introduction

In various parts of the world, acid soils limit crop production and sustainable land use. According to Van Breemen et al. (1984) a soils sensitivity to acidification is determined by its acid neutralizing capacity (ANC) and any amelioration of acid soils must aim at increasing the ANC. In general, this is accomplished through the application of liming materials. However, for many low input production systems the application of lime will not increase the gross margins sufficiently to make the practice economical such as in subsistence based agriculture production systems or in the vast legume based grazing systems of southern and northern Australia (Ridley et al., 1990; Noble et al., 1997; Noble and Randall, 1998).

Several studies have shown that the addition of plant materials to acid soils can increase the soil pH appreciably (Hoyt and Turner, 1975; Asghar and Kanehiro, 1988; Bessho and Bell, 1992; Yan et al., 1996). Only recently, this was clearly attributed to the excess base content of the materials which thus determines their liming potential (Noble et al., 1996; Pocknee and Sumner, 1997; Tang et al., 1999). In search for alternative ways to manage acid soils Noble et al. (1996) and Noble and Randall (1998) have investigated the effects of incorporating leaf litter from different tree species into acidic soils in an 8-week incubation study. Although the observed pH increases were clo-

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sely correlated with the amount of ash alkalinity contained in the litter, the underlying buffering processes were not fully understood or quantified. Various mechanisms for the neutralization of acidity by plant materials with excess cations have been proposed: (1) exchange reactions with base cations (Bessho and Bell, 1992); (2) protonation of added organic anions (Hoyt and Turner, 1975); (3) hydroxyl displacement from sesquioxides by organic anions (Hue and Amiens, 1989); (4) decarboxylation of organic anions (Nätscher and Schwertmann, 1991; Bessho and Bell, 1992; Yan et al., 1996; Pocknee and Sumner 1997).

While exchange and protonation reactions are expected to occur rapidly upon incorporation of the organic materials into the soil, the alkalinity contained in sparingly soluble organic salts or solid organic complexes with base cations will not be available immediately. This alkalinity will only be released upon microbial decarboxylation as described by Nätscher and Schwertmann, (1991) for Ca-oxalate where every proton consumed is accompanied by an equimolar production of CO_2:

$$Ca(COO)_2 + \tfrac{1}{2}O_2 + 2H^+ \rightarrow 2CO_2 + H_2O + Ca^{2+}$$

We have determined the fraction of leaf-litter alkalinity that is readily available for acid neutralization as compared to the alkalinity that is released during the microbial decomposition of organic litter constituents. The buffering processes were examined by relating respiration rates to changes in ANC during an incubation study. Special interest was paid to water-soluble organic materials (DOM) since these components of the added leaf litter are more reactive and bioavailable than insoluble constituents (Williams and Gray, 1974).

2. Materials and methods

2.1. Soil used in study

The soil used in the incubation study was collected in the Book Book district, New South Wales, Australia (35°22' S; 147°30' E) from a pasture supporting subterranean clover and annual volunteer species. Samples were taken from the topsoil (0–10 cm) of an acid red podzolic (Ultic Palexeralf), sieved moist to pass a 2-mm mesh and air-dried. As described by Noble et al. (1996), the pH (10 mM $CaCl_2$) of this silty loam was 3.95 and exchangeable acidity (Al + H) was the dominant component on the exchange complex. In spite of the low pH and high acid saturation, exchangeable Ca made up >30% of the CEC, probably as a result of Ca added in periodic dressings of superphosphate and lime (544 kg ha^{-1}) which was applied 8 y earlier.

2.2. Leaf litter

Freshly fallen leaf litter of two tree species, *Melia azedarach* (white cedar) and *Castanea sativa* (chestnut) was collected in the autumn of 1993 in the vicinity of Canberra. Sugarcane (*Saccharum officinarum*) trash was collected immediately after harvesting in the Herbert River District of north Queensland in 1997. The pH was measured in 1:25 litter: solution ratio of 40 mM KNO_3 after the litter was oven dried at 60°C and ground to a powder. The elemental composition was determined by X-ray fluorescence (XRF) spectrometry (Norrish and Hutton, 1977) and the nitrogen concentration by Kjeldahl digestion and distillation. Total carbon in the litter materials was determined using a CNS-2000 carbon analyzer and the methodology of Matejovic (1996). The ash alkalinity was calculated by difference between the total cations and anions: $\Sigma(Ca^{2+} + Mg^{2+} + K^+ + Na^+) - \Sigma(SO_4^{2-} + H_2PO_4^- + Cl^-)$ based on the elemental composition of the litter. According to Noble et al. (1996) this gives an equally good estimate as titration data. Selected chemical characteristics and pH of each of the litter materials are given in Table 1.

2.3. Incubation experiment

For the incubation study in late 1997, 50 g soil samples were amended with different amounts of the three finely ground litter materials, corresponding to 4, 16 and 32 mg g^{-1} (equivalent to 5, 20 and 40 t ha^{-1} for 10-cm soil depth). In addition, lime treatments of 0.4, 1.6 and 3.2 mg g^{-1} (equivalent to 0.5, 2 and 4 t ha^{-1} of $CaCO_3$) were prepared, thus adding similar amounts of alkalinity as with the *Melia* treatments (Noble et al., 1996). The amended samples and untreated control soil were prepared in triplicate and placed in 250 ml Nalgene screw-top vessels. Immediately before incubation, the samples were thoroughly mixed and moistened to 90% field moisture capacity (15% w/w). During the 20 d incubation at 25°C, CO_2-free air was passed through the vessels for 10 min every h after being stripped of CO_2 by bubbling through 0.1 M NaOH. The efflux from each vessel was passed over a column containing soda lime which was exchanged after 3, 7, 12 and 20 d to determine the trapped CO_2 gravimetrically after drying at 105°C. Background CO_2 was accounted for by including three empty vessels. At the end of the experiment, 8-g aliquots of moist soil were removed from the samples and stored at 5°C until determination of microbial biomass by fumigation-extraction (Vance et al., 1987). The remaining soil was air dried before chemical analysis using the methods outlined in Section 2.4.

2.4. Soil analysis

After incubation of the soils with the various treatments, soluble and exchangeable cations were extracted using 0.1 M $BaCl_2$/0.1 M NH_4Cl (Gillman and Sumpter, 1986) and determined by atomic absorption spectroscopy (Ca and Mg) and flame emission spectroscopy (K and Na). Aluminum was determined by atomic absorption spectroscopy using a nitrous oxide/acetylene flame. Exchangeable H^+ was calculated from pH differences between blanks and soil extracts. Effective CEC was determined from the amount of Mg necessary to replace Ba from the exchange sites according to the method described by Gillman and Sumpter (1986). Exchangeable base cations were then calculated from the difference between CEC and exchangeable acidity (Al + H).

The methodology used to determine the ANC of the soil was a modified discontinuous batch method of James and Riha (1986). In brief, 2-g of air dried soil was shaken in polypropylene tubes containing a total liquid volume of 25 ml and included 0, 0.5, 2.0, 4.0, 10.0 or 20.0 ml of 10 mM HNO_3, 1.0 ml 1 M KNO_3 and 250 μl chloroform. After equilibrating on an end-over-end shaker for 22 h at 25°C, the suspensions were centrifuged and the supernatant pH measured. The ANC ($mmol_c\ kg^{-1}$) was estimated at two pH values, namely 4.0 and 3.0, from plots of equilibrium pH vs mmol (H^+) added kg^{-1}. The ANC of the soils were determined on air dried samples after 20-d incubation. To estimate the 'readily' available ANC due to the addition of litter materials, the ANC was determined on a single composite sample for each treatment of freshly mixed soil and litter prior to being brought to field capacity and incubation.

Water-soluble soil constituents were extracted by shaking 8-g of soil with 40 ml of 1 mM $CaCl_2$ for 2 h, followed by centrifugation and membrane filtration (0.45 μm). Nitrate and ammonium N were determined using autoanalyzer techniques (Markus et al., 1985). Dissolved organic carbon (DOC) was measured with a modified ICP-technique (G. Ridings, personal communication, January 1998). Absorbance of the extracts was measured at 280 nm to estimate the relative aromaticity of the dissolved organic matter (Chin et al., 1994) and at 465 and 665 nm to calculate E_4:E_6 ratios.

2.5. Statistical analysis

Changes in selected soil and biological properties were assessed on data collected at the end of the study using Genstat 5 (Payne, 1993). Preliminary analysis of the soil chemical data was undertaken to determine whether transformation was required to standardise the variances. A simple ANOVA was used to analysis the data where the main effects included in the block treatment model were replication (3), and treatments (a total of 13 treatments). In addition, regression analysis of trends was undertaken on the individual observations.

3. Results

3.1. pH, ANC and CEC

The treatment effects occurring immediately after mixing the amendments with soil are listed in Table 2. As expected, the addition of lime resulted in rapid pH increases relative to the application rates. Relative to the unamended control, $ANC_{pH\ 3}$ increased by 9, 25 and 65 $mmol_c\ kg^{-1}$ and $ANC_{pH\ 4}$ increased by 8, 30 and 60 $mmol_c\ kg^{-1}$. Except for the $ANC_{pH\ 3}$ at the second treatment level, these values are in good accordance (±10%) with the added amounts of alkalinity (Table 2). The increase in CEC at the two highest liming treatments is attributed to pH-dependent charge generation associated with organic and inorganic exchange sites.

Of the litter materials, *Melia* had the most pronounced immediate effect on soil properties. $ANC_{pH\ 3}$ increased by 5, 22 and 45 $mmol_c\ kg^{-1}$ at the three treatment rates, corresponding to 44, 48 and 49% of the calculated added ash alkalinity (Table 2). In contrast, $ANC_{pH\ 4}$ was less affected by *Melia* treatments, being only 4, 12 and 18 $mmol_c\ kg^{-1}$ higher than the control. The CEC was not affected by *Melia*-additions, while base saturation increased slightly in the higher amendment levels (Table 2). In the *Castanea* treatments, pH, CEC, base saturation and $ANC_{pH\ 4}$ were not affected prior to incubation, while $ANC_{pH\ 3}$ increased in response to the added rates of litter by amounts equivalent to 71, 53 and 51% of the added

Table 1
Chemical composition of the litter materials from the different plant species

Plant species	Ash alkalinity ($mmol_c\ kg^{-1}$)	Ca (%)	pH[a]	Total C (%)	Total N (%)	C:N ratio
Sugarcane	334	0.39	5.61	46.1	0.48	96
Melia azedarach	2878	4.64	5.52	44.2	0.99	44
Castanea sativa	1409	1.86	4.46	49.5	0.48	103

[a] pH measured in 1:25 litter: solution ratio of 40 mM KNO_3.

Table 2
Amounts of alkalinity added with lime and leaf litter and their effects on pH, ANC, CEC and base saturation (BS) before ($n = 1$) and after incubation ($n = 3$)

	Added alkalinity ($mmol_c\ kg^{-1}$)	pH[a]	Before incubation				pH	After incubation			
			ANC_{pH3} ($mmol_c\ kg^{-1}$)	ANC_{pH4} ($mmol_c\ kg^{-1}$)	CEC ($mmol_c\ kg^{-1}$)	BS (%)		ANC_{pH3} ($mmol_c\ kg^{-1}$)	ANC_{pH4} ($mmol_c\ kg^{-1}$)	CEC ($mmol_c\ kg^{-1}$)	BS (%)
Control		3.9	25	−2	23	41	4.0	26	−1	27	48
Lime	8.0	4.3	34	6	22	64	4.4	35	6	28	83
	32.0	5.9	50	28	32	81	5.6	53	25	38	98
	64.0	6.6	90	58	40	100	6.7	87	48	47	99
Castanea	5.6	4.0	29	0	23	42	4.1	30	2	24	55
	22.6	4.0	37	0	23	40	4.5	39	9	22	67
	45.1	4.0	48	0	26	39	4.5	47	10	25	66
Melia	11.5	4.1	30	2	22	41	4.4	34	6	25	70
	46.0	4.5	47	10	24	50	5.5	56	22	29	94
	92.1	4.7	70	16	24	46	6.0	87	42	38	98
Sugarcane	1.3	3.9	25	−2	19	32	4.0	26	−1	26	54
	5.3	3.9	27	0	19	27	4.2	32	4	23	57
	10.7	4.2	33	3	17	33	4.4	32	4	15	46
$LSD_{0.05}$ (after)		ND	ND	ND	ND	ND	0.1	3	2	4	7

[a] pH measured in 50 mM KNO_3 1:25 soil:solution ratio; ND, not determined.

alkalinity (Table 2). Sugarcane trash, which had the lowest alkalinity of all the litter materials had the least effect on these properties and even resulted in a reduction in CEC and base saturation over all three levels of treatment (Table 2).

Soil incubation for 20-d had only minor effects on pH, ANC and CEC in the lime treatments but caused distinct changes in the different organic amendments (Table 2). In all soils that received the two higher amounts of litter addition, pH increased after incubation, most markedly in the *Melia* treatment and least with sugarcane. The observed pH increases were accompanied by equivalent changes in $ANC_{pH\ 4}$ in all treatments, which is also reflected in the close relationship between these variables before or after incubation (Fig. 1).

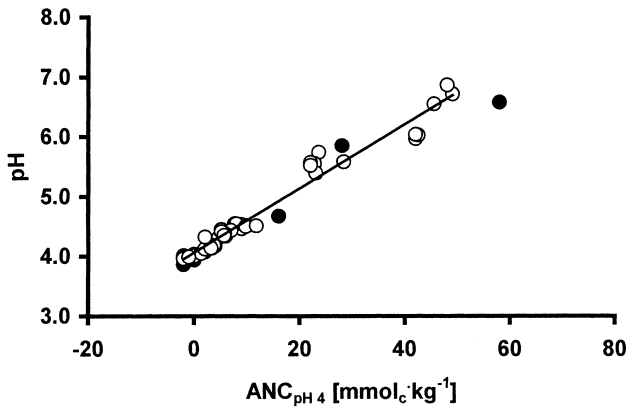

Fig. 1. Relationship between $ANC_{pH\ 4}$ and pH (in 0.04 M KNO_3) of all treatments before (●) and after 20-d of incubation (○). The regression was only fitted to the data points after incubation ($y = 0.54x + 4.06$, $R^2 = 0.97$).

In the *Castanea* and sugarcane amended soils, $ANC_{pH\ 3}$ remained almost the same as before incubation (Table 2), showing that no additional alkalinity was generated through the microbial mineralization processes. But in all *Castanea* treatments, more acid was required to lower the soils pH to four than before incubation and consequently, the further acidification of the soil samples from pH 4 to pH 3 required less acid ($ANC_{pH\ 3}$–$ANC_{pH\ 4}$ decreased). This suggests, that weaker acidic groups increased at the expense of stronger acidic groups.

With *Melia*, both ANC values increased during incubation (Table 2), indicating that additional buffering agents were made available. At the two higher amendment rates, incubation-induced changes were greater in $ANC_{pH\ 4}$ than in $ANC_{pH\ 3}$ (+12 vs +9 $mmol_c\ kg^{-1}$ and +22 vs +17 $mmol_c\ kg^{-1}$). As a consequence, the differences between $ANC_{pH\ 3}$ and $ANC_{pH\ 4}$ decreased during incubation from 37 to 34 $mmol_c\ kg^{-1}$ at the second treatment level and from 53 to 45 $mmol_c\ kg^{-1}$ at the third treatment level (Table 2). This shows that strongly acidic groups have actually declined during incubation, similar to the *Castanea* treatments. The observed increases in ANC are therefore due to the direct consumption of H^+ or due to the production or release of buffering agents that neutralize acid at pH > 3.

Compared to inputs with *Melia* litter, incubation-induced increases in $ANC_{pH\ 4}$ amount to 17, 22 and 26% of the added alkalinity at the three treatment levels. Together with the initial litter effects, the total $ANC_{pH\ 4}$ increase over control values is equivalent to

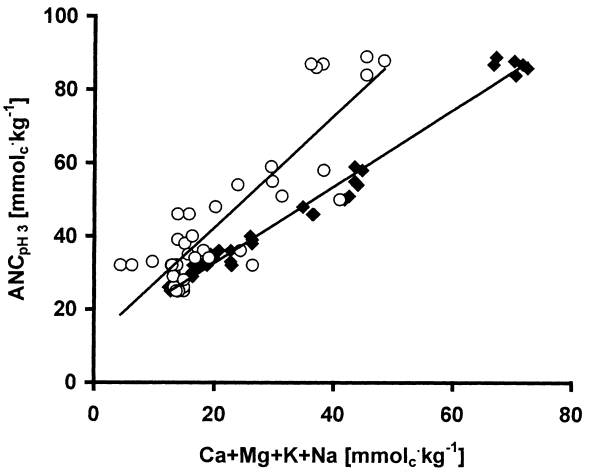

Fig. 2. Relationship between $ANC_{pH\,3}$ and exchangeable (○) or extractable (◆) basic cations in all treatments at the end of the 20-d incubation. The fitted regression lines are $y = 1.53x + 11.81$ ($R^2 = 0.77$) for the exchangeable and $y = 1.05x + 11.76$ ($R^2 = 0.98$) for the extractable cations.

roughly 50% of the added alkalinity at all levels. If $ANC_{pH\,3}$ is considered, 67–78% of litter alkalinity were available for acid buffering after incubation, compared to the initial 43–49%.

Both $ANC_{pH\,3}$ and $ANC_{pH\,4}$ are correlated with exchangeable base cations ($R = 0.88$ and 0.92, respectively). However, this does not explain the observed increases in ANC, since the slope of the linear relationship between the two variables is well beyond unity (Fig. 2). In the *Castanea* treatments, ANC increased significantly over control values, while exchangeable base cations remained unchanged (Table 2).

In the $BaCl_2/NH_4Cl$ extracts from the treated soils, the total sum of base cations generally exceeded the amount of exchangeable base cations considerably (Fig. 3). This indicates the presence of soluble salts which apparently contribute to the neutralization of acidity as shown by the close correlation between total extractable base cations and $ANC_{pH\,3}$ ($R = 0.99$), and the fact that the slope of the line is very close to unity (Fig. 2). A similarly close relationship was found for $ANC_{pH\,4}$ with a slope of 0.79 (not shown) suggesting that at this higher pH not all extractable base cations participate in buffering.

The treatment effects on extractable base cations were also evaluated by comparing base cation inputs with the increase in extractable base cations over the control. These calculations show, that in the lime treatments, Ca inputs were extracted almost quantitatively (89–101%) after incubation (Fig. 3). These values are similar to the values before incubation (88–103%) and indicate that $CaCO_3$ dissolves readily and is not immobilized by biological activity. In the soils amended with *Castanea*, 46–54% of the base cation inputs were retrieved in the extracts before and 49–63% after incubation. Exchangeable base cations were not affected by this treatment (Fig. 3). In the *Melia* treatments, 58–68% of the base cation inputs were extractable before and similarly 57–64% after incubation. However, the amounts of exchangeable base cations increased during incubation from 10–15% of the inputs to 25–37%, corresponding to the increase in CEC (Table 2). In the sugarcane treatments, base cation inputs were readily extractable immediately after mixing (66–78%), and decreased slightly during incubation to 57–61%. But despite these higher base cation availabilities, the amounts of exchangeable base cations after incubation

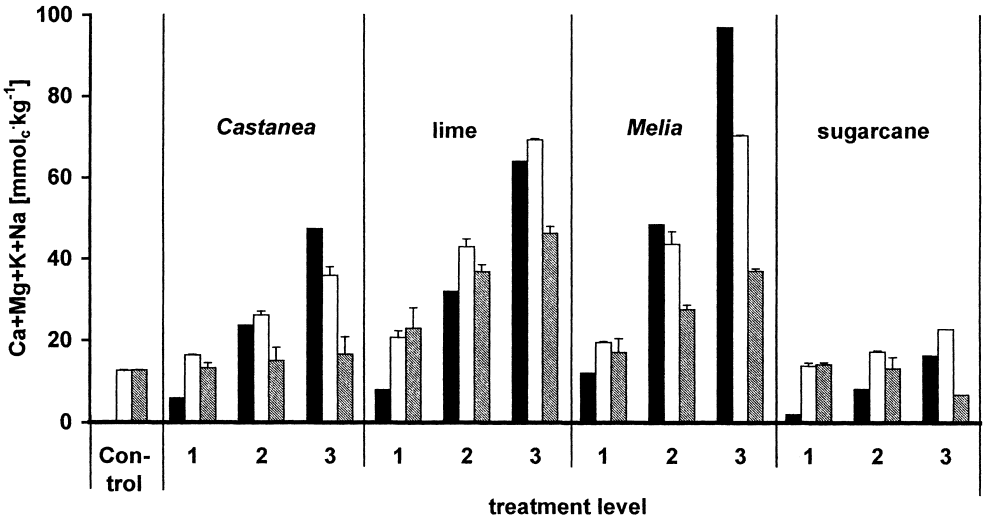

Fig. 3. Calculated inputs of basic cations with the different treatments (black), $BaCl_2$-extractable basic cations (white) and exchangeable basic cations (hatched) at the end of the 20-d incubation (means of three replicates with SD).

decreased with increasing amendment rates (Fig. 3), similar to the treatment effects on CEC (Table 2).

The contribution of N mineralization processes to the acid balance in the soils was evaluated by comparing extractable mineral N-forms before and after incubation. However, net N-mineralization was only observed in the control and lime treatments, in all litter treatments, the initially available mineral N forms were depleted to concentrations close to detection limits during incubation. As a consequence, a net acid consumption was calculated as −0.5 to −0.8 mmol H^+ kg^{-1}. When compared with the ANC-increases of 2 to 62 $mmol_c$ kg^{-1}, these N mineralization processes have no major influence on acid neutralization.

3.2. Biological activity and microbial biomass

Microbial respiration was stimulated by all treatments and increased with amendment rates (Table 3). In general, CO_2 evolution was highest during the first 3-d of incubation (28.5–61.1 mg CO_2 kg^{-1} h^{-1} in the highest litter treatments) and then declined rapidly reaching only 8–25% of the initial values during the last 6-d of incubation. No such dynamics were observed in the control (< 2 mg CO_2 kg^{-1} h^{-1} during the entire 20-d incubation). In the lime treatments, most CO_2 probably stems from the added lime, but the higher microbial biomass-C (Table 3) also suggests increased contributions from microbial respiration.

In the organic amendments, mineralization rates were calculated assuming that all excess CO_2-production over the control resulted from the added materials. Total respiration and mineralization rates were highest in the *Melia* treated soils and correspond well with microbial biomass C (Table 3). A close relationship between cumulative CO_2 release and change in $ANC_{pH\ 4}$ was observed for *Melia* (Fig. 3). For the other two litter amendments (*Castanea* and sugarcane) a similar relationship can not be established since the increased CO_2 evolution at higher amendment rates was not associated with concomitant changes in ANC (Fig. 3).

3.3. Water-extractable organic carbon

Initially, all treatments increased the amount of soluble organic carbon in the $CaCl_2$ extracts (Table 4). In the litter treatments, this soluble organic fraction is specific for the different species and amounts to 32–36% of the added C_{org} for *Melia*, 17–19% for *Castanea* and 7–8% for sugarcane. The spectroscopic properties of the extracts indicate that the DOC released in the *Melia* treatments is generally less aromatic (lower ϵ_{280}) and smaller in molecular size (higher E_4:E_6) than in the control. This contrasts with *Castanea*, where the decreasing E_4:E_6-ratios at the higher amendment rates indicate larger molecules with relatively high specific absorbance at 280 nm (Table 4).

After 20-d of incubation, the amount of extractable organic carbon declined considerably in all treatments except the control (Table 4). In the litter amendments, the loss of DOC is almost equivalent to cumulative respiration rates as shown by a slope close to unity between the two variables (Fig. 4). Thus, CO_2 pro-

Table 3
C_{org}-inputs, cumulative CO_2-evolution, mineralization rates and microbial biomass at the end of the incubation of the different treatments (n = 3)

Treatment level	C_{org} input (mmol kg^{-1})	Cumulative CO_2-evolution (mmol kg^{-1})	Mineralization rate (% of C_{org} input)	Microbial biomass-C (mmol kg^{-1})
Control	0	8	–	3.4
Lime				
1	0	11	–	4.7
2	0	18	–	6.8
3	0	46	–	11.0
Castanea				
1	165	42	26	3.4
2	660	93	14	9.5
3	1320	140	11	18.4
Melia				
1	147	47	32	4.7
2	589	137	23	11.6
3	1179	226	19	22.8
Sugarcane				
1	154	21	14	5.3
2	615	66	11	5.8
3	1229	101	8	5.3
$LSD_{0.05}$	ND[a]	23	ND	ND

[a] ND, not determined.

Table 4
DOC-concentrations and spectroscopic properties of 1 mM $CaCl_2$ extracts of the treatments before ($n = 1$) and after incubation ($n = 3$)

Treatment level		Before incubation			After incubation		
		DOC (mM)	ϵ_{280}[a]	$E_4:E_6$[b]	DOC (mM)	ϵ_{280}[a]	$E_4:E_6$[b]
Control		1.3	105	0.8	2.2	145	2.2
Lime	1	2.8	71	2.0	2.6	176	2.3
2	5.4	52	2.1		3.9	223	2.7
3	12.9	26	2.3		9.0	194	3.0
Castanea	1	6.8	81	2.2	3.3	164	2.4
2	21.7	104	1.7		7.8	145	2.6
3	42.3	69	1.6		13.6	127	2.7
Melia	1	9.2	103	2.5	3.3	186	2.4
2	34.6	79	3.3		8.4	155	2.6
3	61.1	41	4.2		20.3	107	3.0
Sugarcane	1	4.6	59	1.9	2.4	129	2.3
2	10.0	58	2.1		3.2	136	2.3
3	21.8	49	2.4		3.8	147	2.4
$LSD_{0.05}$ (after)	ND	ND	ND		2.0	39	0.1

[a] Specific absorbance of DOC at 280 nm [l $mmol^{-1}$ m^{-1}].
[b] Absorbance ratio at 465:665 nm. ND not determined.

duction could be fully accounted for by the mineralization of soluble organic compounds introduced with the litter.

During incubation, specific absorbance at 280 nm increased in all extracts after incubation (Table 4), indicating an increased aromaticity of the remaining soluble organic fraction compared to the fresh extracts and thus a preferential degradation of the soluble aliphatic structures. The $E_4:E_6$ ratios in the extracts increased to various degrees in most treatments. Only in the *Melia* amended soils did the $E_4:E_6$ ratios decrease during incubation.

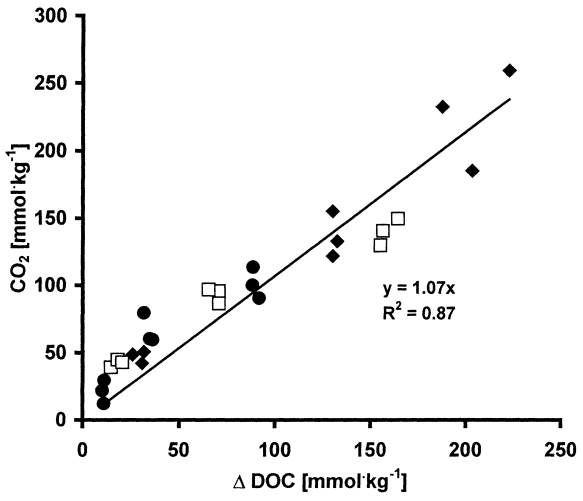

Fig. 4. Relationship between the change in extractable soluble organic compounds (DOC) and total CO_2 evolution in all replicates of the different treatments (◆, *Melia*; □, *Castanea*; ●, sugarcane).

4. Discussion

The immediate increase in ANC after mixing leaf litter with soil shows that some of the added ash alkalinity is present in a readily available form that is released independent of mineralization processes. As shown by the small effects of the litter materials on CEC and base saturation, this rapid buffering is not due to simple exchange reactions as proposed by Bessho and Bell (1992). Instead, protonation of organic anions and functional groups (Hoyt and Turner, 1975) seems to be the predominant buffering process at this stage. In the *Castanea* treatments, increased buffering only occurs below pH 4 and, therefore, is associated with strongly acidic functional groups or organic acids having a $pK_a < 4.0$ (Nätscher and Schwertmann, 1991) as found typically for carboxyl groups (Blaser et al., 1984). In the *Melia* treatments, weaker acidic groups must also be present, as initial buffering was also elevated above pH 4 (Table 2). The pH-increase in the two higher level *Melia*-treated soils would thus be explained by direct H^+ consumption through protonation of these weak acids.

These immediately available organic buffering substances may be largely present as organic salts of base cations which are extractable with $BaCl_2$ and thus cause the large surplus of base cations in these extracts compared to the amounts present in exchangeable form. Various low molecular organic acids and salts such as amino acids, oxalate, malate, acetate and citrate are present in leaves (Browne, 1995) and most have pK_a values around or below 4.0 (Lide and Frederikse, 1995). The importance of soluble compounds for direct buffering was also shown by Asghar and

Kanehiro (1988), who observed a 40% decrease in ANC of sugarcane after it was leached with water. These dissolved organic compounds probably also contribute to the high DOC concentrations in the initial soil extracts from the litter treatments.

In the litter amended soils, the initial effect on ANC was generally higher than the subsequent increase in ANC during the 20-d incubation. However, in the *Melia* and *Castanea* treatments, major changes in the nature of the buffering substances during incubation are indicated by a shift from the initial predominance of strong acid groups to an increased acid neutralization capacity above pH 4 combined with pH increases. As shown by Pocknee and Sumner (1997) such pH increases are clearly due to the decarboxylation of organic compounds containing basic cations. In this process, H^+ is consumed and the basic cations become available for exchange reactions as it is reflected in the increased base saturation of the *Castanea* and *Melia* treatments. Thus, strong acid groups such as carboxyl are mineralized and no longer available for buffering at low pH.

The close relationship between CO_2 evolution and DOC disappearance indicates that microbial decomposition processes in these treatments preferentially consumed the soluble fraction of the added litter materials. Other studies have shown that fresh leaf litter extracts largely consist of highly bioavailable low molecular compounds such as amino acids, amino sugars, simple sugars, polysaccharides and proteins which strongly influences the initial stages of litter decomposition (Williams and Gray, 1974; Blaser et al., 1984; Guggenberger et al., 1989; Kuiters, 1992). Despite their bioavailability, these soluble organics had not been fully depleted in all treatments by the end of the experiment. The continuously decreasing respiration rates suggest, that the remaining soluble compounds are less degradable. This is supported by the increasing ϵ_{280} values that indicate an accumulation of aromatic compounds which are more resistant to microbial attack (Paul and Clark, 1989). In the *Melia*-treated soils, declining E_4:E_6-ratios suggest that this is accompanied by an accumulation of larger, less acidic DOM-molecules (Chen et al., 1977). In the other two litter treatments, qualitatively different decomposition processes appear to be responsible for the increasing E_4:E_6-ratios during incubation.

A strong decline in decomposition rate after this initial phase would further reduce the release of alkalinity from the litter. For *Melia*, data from an 8-week incubation (Noble et al., 1996) suggested that no further increase in pH or exchangeable Ca occurs during that extended period. This indicates that the remaining 20–30% of ash alkalinity in the litter are associated with compounds or structures that are more persistent. Possibly, nitrogen availability is a limiting factor in the decomposition process as indicated by the negative net-N mineralization in all litter amended soils and by the positive relationship between N-content and final pH in the incubation studies of Noble and Randall (1998).

From a practical perspective, a more stable pool of potentially available alkalinity can be considered beneficial for the remediation of soil acidity since it is protected from leaching losses. However, for this pool of alkalinity to be effective, it would need to be released over the long term. For the amelioration of acid soils through the introduction of externally produced organic materials containing excess basic cations, this is of minor importance. If only topsoil acidity is considered, a similar effect may be obtained by deep rooting plants, that 'pump' alkalinity from deeper soil layers and store it in their foliage. With litter-fall and subsequent release of ash alkalinity, ANC and eventually pH would increase in the topsoil. This would thus lead to a redistribution of alkalinity within the soil profile. However, the basic cations need to be fully released through mineralization as the accumulation of non-exchangeable basic cations in the organic matter of forest floors are the main reason for soil acidification if the soil is poor in alkalinity (Mahendrappa et al., 1986; Vogt et al., 1986).

5. Conclusions

This study has shown that the liming potential of organic amendments for reducing soil acidity is primarily determined by their ash alkalinity. The release of buffering substances from the litter materials is initially not effective in increasing pH or base saturation since basic cations are largely associated with strong acidic organic functional groups. For short-term acid neutralization, mineralization of soluble organic compounds containing basic cations seems to be the most important process. Effects of N mineralization on acidity changes were not relevant due to the low N content of the materials used. Instead, nitrogen availability appears to be a limiting factor in the decomposition process and could have therefore restricted the microbial release of alkalinity.

Using ANC as a measure for soil acidity allows one to directly quantify the contribution and release of ash alkalinity by the litter materials. Although ANC is closely related to the amount of exchangeable basic cations, it also quantifies changes in variable charge and thus is particularly important in evaluating the acidity changes in highly weathered tropical soils or organic soil horizons. Furthermore, the simple determination of a buffer curve allows one to differentiate between different strengths of acidity present in the soil which

determines the pH change and gives further information about the buffering substances.

A short-term evaluation of ash alkalinity release from leaf litter as in our study may not be sufficient to predict longer term effects, as shown by Madeira (1988). He reported that leachates from *Eucalyptus globulus* leaf litter were much more effective than *Quercus suber* leachates in increasing the base status of a soil. But in plantations, soil acidification was higher under *Eucalyptus* because more litter accumulated than under *Quercus*. Therefore, longer-term field studies would be necessary in order to evaluate the potential of on-site amelioration of soil acidity by deep rooting tree species.

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References

Asghar, M., Kanehiro, Y., 1988. Effects of sugarcane trash and pineapple residue on titration curves, redox potential and extractable Mn and Fe in an oxisol. Biological Wastes 24, 27–38.

Bessho, T., Bell, L.C., 1992. Soil and solution phase changes and mung bean response during amelioration of aluminum toxicity with organic matter. Plant and Soil 140, 183–196.

Blaser, P., Sposito, G., Holtzclaw, K.M., 1984. Composition and acid functional group chemistry of an aqueous chestnut leaf litter extract. Soil Science Society of America Journal 48, 278–283.

Browne, B.A. 1995. Towards a new theory of podzolisation. In: McFee, W.W., Kelly, J.M. (Eds.), Carbon Form and Function in Forest Soils. Soil Science Society of America, Madison, pp. 253–273.

Chen, Y., Senesi, N., Schnitzer, M., 1977. Information provided on humic substances by E4/E6 ratios. Soil Science Society of America Journal 41, 352–358.

Chin, Y.P., Aiken, G., O'Loughlin, E., 1994. Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. Environmental Science and Technology 28, 1853–1858.

Gillman, G.P., Sumpter, E.A., 1986. Modification to the compulsive exchange method for measuring exchange characteristics of soils. Australian Journal of Soil Research 24, 61–66.

Guggenberger, G., Kögel-Knabner, I., Haumeier, L., Zech, W., 1989. Gel permeation chromatography of water soluble organic matter with deionized water as eluent. II. Spectroscopic and chemical characterization of fractions obtained from an aqueous litter extract. Science of the Total Environment 81, 447–457.

Hoyt, P.B., Turner, R.C., 1975. Effects of organic materials added to very acid soils on pH, aluminum, exchangeable NH_4, and crop yields. Soil Science 119, 227–237.

Hue, N.V., Amiens, I., 1989. Aluminum detoxification with green manures. Communications in Soil Science and Plant Analysis 20, 1499–1511.

James, B.R., Riha, S.J., 1986. pH buffering in forest soil organic horizons: relevance to acidic deposition. Journal of Environmental Quality 15, 458–462.

Kuiters, A.T.M.W., 1992. Gel permeation chromatography and Cu-binding of water-soluble organic substances from litter and humus layers of forest soil. Geoderma 52, 1–15.

Lide, D.R., Frederikse, H.P.R., 1995. CRC Handbook of Chemistry and Physics, 76th ed. CRC Press, Boca Raton.

Madeira, M.A.V., 1988. Changes in soil properties under Eucalyptus plantations in Portugal. In: Pareira, J.S., Landslung, J.J. (Eds.), Biomass Production by Fast-Growing Trees, NATO ASI-Series, Series E: Applied Sciences, vol. 166, pp. 81–99.

Mahendrappa, M.K., Foster, N.W., Weetman, G.F., Krause, H.H., 1986. Nutrient cycling and availability in forest soils. Canadian Journal of Soil Science 66, 547–572.

Markus, D.K., McKinnon, J.P., Buccafuri, A.F., 1985. Automated analysis of nitrite, nitrate and ammonium N in soils. Soil Science Society of America Journal 49, 1208–1215.

Matejovic, I., 1996. The application of Dumas method for the determination of carbon, nitorgen and sulphur in plant samples. Rostlinna Vyroba 42, 313–316.

Nätscher, L., Schwertmann, U., 1991. Proton buffering in organic horizons of acid forest soils. Geoderma 48, 93–106.

Noble, A.D., Randall, P.J., 1998. The Impact of Trees and Fodder Shrubs on Soil Acidification. Rural Industries Research and Development Corporation, Canberra, ACT.

Noble, A.D., Zenneck, I., Randall, P.J., 1996. Leaf litter ash alkalinity and neutralisation of soil acidity. Plant and Soil 179, 293–302.

Noble, A.D., Cannon, M., Muller, D., 1997. Evidence of accelerated soil acidification under *Stylosanthes*-dominated pastures. Australian Journal of Soil Research 35, 1309–1322.

Norrish, K., Hutton, J.T., 1977. Plant analysis by X-ray spectrometry. X-Ray Spectrometry 6, 6–11.

Paul, E.A., Clark, F.E., 1989. Soil Microbiology and Biochemistry. Academic Press, San Diego.

Payne, R.W., 1993. Genstat 5. Release 3. Oxford University Press, Oxford.

Pocknee, S., Sumner, E., 1997. Cation and nitrogen contents of organic matter determines its liming potential. Soil Science Society of America Journal 61, 86–92.

Ridley, A.M., Helyar, K.R., Slattery, W.J., 1990. Soil acidification under subterranean clover (*Trifolium subterraneum*) pastures in north-eastern Victoria. Australian Journal of Experimental Agriculture 30, 195–201.

Tang, C., Sparling, G.P., McLay, C.D.A., Raphael, C., 1999. Effect of short-term legume residue decomposition on soil acidity. Australian Journal of Soil Research 37, 561–573.

Van Breemen, N., Driscoll, C.T., Mulder, J., 1984. Acidic depositions and internal proton sources in acidification of soils and water. Nature 307, 422–424.

Vance, E.D., Brookes, P.C., Jenkinson, D.S., 1987. An extraction method for measuring soil microbial biomass C. Soil Biology and Biochemistry 19, 703–707.

Vogt, K.A., Grier, C.C., Vogt, D.J., 1986. Production, turnover, and nutrient dynamics of above-and below-ground detritus of world forests. Advances in Ecological Research 15, 303–377.

Williams, S.T., Gray, T.R.G. 1974. Decomposition of litter on the soil surface. In: Dickinson, C.H., Pugh, G.J.F. (Eds.), Biology of Plant Litter Decomposition. Academic Press, New York, pp. 611–632.

Yan, F., Schubert, S., Mengel, K., 1996. Soil pH increase due to biological decarboxylation of organic anions. Soil Biology and Biochemistry 28, 617–624.