Available online at www.sciencedirect.com

SCIENCE DIRECT

Agriculture, Ecosystems and Environment 100 (2003) 161–171

Agriculture Ecosystems & Environment

www.elsevier.com/locate/agee

Cation exchange capacities of soil organic matter fractions in a Ferric Lixisol with different organic matter inputs

K. Oorts [a,*], B. Vanlauwe [b,1], R. Merckx [a]

[a] *Laboratory of Soil Fertility and Soil Biology, Faculty of Applied Agricultural Sciences,*
Kasteelpark Arenberg 20, 3001 Leuven/Heverlee, Belgium
[b] *Soil Microbiology Unit, International Institute of Tropical Agriculture (IITA), Ibadan, Nigeria,*
c/o Lambourn, Carolyn House, 26 Dingwall Road, Croydon CR9 3EE, UK

Abstract

Soil organic matter (SOM) has an important effect on the physicochemical status of highly weathered soils in the tropics. This work was conducted to determine the contribution of different SOM fractions to the cation exchange capacity (CEC) of a tropical soil and to study the effect of organic matter inputs of different biochemical composition on the CEC of SOM. Soil samples were collected from a 20-year-old arboretum established on a Ferric Lixisol, under seven multipurpose tree species: *Afzelia africana*, *Dactyladenia barteri*, *Gliricidia sepium*, *Gmelina arborea*, *Leucaena leucocephala*, *Pterocarpus santalinoides*, and *Treculia africana*. Fractions were obtained by wet sieving and sedimentation after ultrasonic dispersion. Relationships between CEC and pH were determined using the silver thiourea-method and were described by linear regression. The CEC of the fractions smaller than 0.053 mm was inversely related to their particle size: clay (<0.002 mm) $>$ fine silt (0.002–0.02 mm) $>$ coarse silt (0.02–0.053 mm), except for the soils under *T. africana*, *D. barteri*, and *L. leucocephala*, where the CEC of the fine silt fraction was highest or comparable to the CEC of the clay fraction. The clay and fine silt fractions were responsible for 76–90% of the soil CEC at pH 5.8. The contribution of the fine silt fraction to the CEC at pH 5.8 ranged from 35 to 50%, which stressed the importance of the fine silt fraction for the physicochemical properties of the soil. Differences in CEC between treatments for the whole soil and the fractions could be explained by the differences in carbon content. Except for the intercept for the clay fraction, SOM had a significant ($P < 0.001$) contribution to both the intercepts (=estimated CEC at pH 0) and slopes (=pH-dependent charge) of the CEC–pH relationships for the whole soil and the fractions. The CEC of SOM at pH 5.8 varied between 283 $\mathrm{cmol_c\,kg^{-1}}$ C for particulate organic matter, and 563 $\mathrm{cmol_c\,kg^{-1}}$ C for the fine silt fraction. The biochemical composition of the organic inputs did not have an important effect on the CEC of SOM. In total, SOM was responsible for 75–85% of the CEC of these soils.

Keywords: Cation exchange capacity; Soil organic matter; Particle size fractions; Lixisol

---

1. Introduction

In many soils in the tropics, weathering has reached an advanced stage, resulting in clay minerals with low nutrient retention capacities. Typical values for the cation exchange capacity (CEC) of soils dominated by kaolinite and amorphous oxides range from

---

* Corresponding author. Tel.: +32-16-321630;
fax: +32-16-321997.
E-mail address: koen.oorts@agr.kuleuven.ac.be (K. Oorts).

[1] Present address: Tropical Soil Biology and Fertility Program, Unesco-Gigiri, PO Box 30597, Nairobi, Kenya.

0167-8809/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0167-8809(03)00190-7

2 to 6 $\mathrm{cmol_c\,kg^{-1}}$ (Gallez et al., 1976; Duxbury et al., 1989). As permanent charge in these soils is generally only 1 or 2 $\mathrm{cmol_c\,kg^{-1}}$, the importance of the CEC due to variable charge is obvious (Gallez et al., 1976; Oades et al., 1989). Variable charge is associated primarily with oxides and soil organic matter (SOM). As oxides mainly express positive charges at the natural soil pH, due to their high 'point of zero variable charge' ($\mathrm{pH_0}$), SOM is the most important contributor to the CEC in these soils. Generally, SOM is responsible for 25–90% of the total CEC of surface horizons of mineral soils (Van Dijk, 1971; Oades et al., 1989). The role of SOM in determining the sign and magnitude of the net charge and, therefore, in the retention of plant nutrients, emphasizes the need for management systems designed to maintain high levels of organic matter in tropical soils (Morais et al., 1976; Oades et al., 1989).

In view of its complex nature, many studies have attempted a systematic fractionation of SOM in order to relate observed differences in the biological lability of SOM with differences in chemical or physical properties of homogeneous SOM fractions (Christensen, 1992). Recent efforts in characterizing SOM rely on fractionation schemes based on particle size and/or density. This approach emphasizes the role of soil minerals in SOM stabilization and turnover, and is considered less destructive than the "traditional" chemical fractionations. The results obtained are thought to relate more directly to the structure and function of SOM in situ (Christensen, 1992). The effectiveness of such physical fractionations depends to a large extent on the soil dispersion procedure. Since chemical dispersion procedures may introduce unintended in-process changes of SOM structure and distribution, ultrasonic dispersion is preferred for studies on organomineral complexes. Therefore, when studying charge properties of SOM, a physical fractionation through ultrasonic dispersion, sieving, sedimentation, and flotation may be preferred.

The objectives of this study were to: (i) determine the contribution of the different particle size fractions to the CEC of the soil, (ii) assess the CEC–pH relationship of SOM in the different particle size fractions, and (iii) determine the effect of the biochemical composition of the organic matter inputs on the CEC of SOM.

2. Materials and methods

2.1. Site description

Soil was collected from a multipurpose tree arboretum, established in 1979, at the International Institute of Tropical Agriculture (IITA) in Ibadan, southwestern Nigeria (3°54′E and 7°30′N). The area has a bimodal rainfall, with an annual mean of 1278 mm and a mean annual temperature of 26 °C. The site has an average slope of 5%. The soil is a Ferric Lixisol (USDA: Oxic Paleustalf). This soil is formed on banded gneiss derived from pre-Cambrian basement complex rocks. The clay from the upper horizons contains more than 60% kaolinite and some mica, goethite, and hematite (Gallez et al., 1975). The arboretum consists of unreplicated plots each of which has a size of 12 m width by 20 m length and consists of five rows of six trees of the same species. Litter was always left on the surface and weed growth was strongly suppressed, so SOM originates almost completely from tree litterfall (about 4.5–9.5 t dry matter $\mathrm{ha^{-1}}$ per year; Kang and Akinnifesi, 1994).

Soil samples were taken in March 1999 from the surface horizons (0–10 cm) of seven different plots, under the following trees: *Afzelia africana*, *Dactyladenia barteri*, *Gliricidia sepium*, *Gmelina arborea*, *Leucaena leucocephala*, *Pterocarpus santalinoides*, and *Treculia africana*. In each plot, four soil cores of 10 cm depth and 10 cm diameter were randomly sampled at different locations in each alley. The samples from different alleys in a plot were kept apart as plot replicates. Litter was collected from the soil surface before soil sampling. The soil samples were air-dried, and passed through a 4 mm sieve to remove roots and large stones before fractionation. Leaves were collected from the different tree species. Litter and leaf samples were air-dried before analysis.

2.2. Fractionation

The soil organic matter fractions used in this study were obtained by physical fractionation after ultrasonic dispersion. Ultrasonic dispersion was preferred in order to avoid any possible artefact on the CEC that could be caused by the use of chemicals during the dispersion. Soil suspensions (25 g soil + 125 ml distilled water) were treated for 10 min at 62.5 W

(=1500 J g^{-1} soil) with a Misonix Sonicator®, model XL2020. The soil suspensions were then separated into the following particle size classes: >2 mm, 0.25–2 mm, and 0.053–0.25 mm, using a wet sieving shaker (Fritsch ®analysette3, 50 Hz, 1.5 mm amplitude). The fractions on the sieves were collected and further fractionated into mineral and organic material through flotation on water. Soil particles smaller than 0.053 mm were collected in a bucket and manually sieved with a 0.020 mm screen. The fine silt fraction (0.002–0.020 mm) was separated from a subsample of the material smaller than 0.020 mm through four sedimentation cycles (based on Stokes' Law: room temperature, 11.6 cm of soil slurry, 8 h; Gee and Bauder, 1986). The clay fraction (<0.002 mm) in the combined supernatants was concentrated by flocculation with $CaCl_2$ (final concentration: about 0.02 M). The flocculated clay suspension was separated from the clear supernatant, transferred to a dialysis membrane (Spectra/Por® 4, MWCO 12-14,000) and washed free of salts with distilled water. All fractions were dried overnight at 60 °C and weighed.

This fractionation scheme resulted in the following nine fractions: 2–4 mm mineral: 'M2000'; 2–4 mm organic: 'O2000'; 0.250–2 mm mineral: 'M250'; 0.250–2 mm organic: 'O250'; 0.053–0.250 mm mineral: 'M53'; 0.053–0.250 mm organic: 'O53'; 0.020–0.053 mm mineral and organic: 'coarse silt'; 0.002–0.020 mm mineral and organic: 'fine silt'; and <0.002 mm mineral and organic: 'clay'. Dry weight recovery in the nine fractions ranged from 98.2 to 99.6%.

2.3. Analysis of soil and plant samples

The pH of the soil was measured in a 0.01 M $CaCl_2$ solution at a 1:5 soil:solution weight ratio. Organic carbon and total nitrogen contents of soil and plant samples were determined using a CN analyzer-mass spectrometer (ANCA-GSL Preparation Module + 20-20 Stable Isotope Analyzer, Europa Scientific) after pulverization. Plant material was analyzed for its lignin and cellulose content by the acid detergent fiber method (Van Soest, 1963; Van Soest and Wine, 1967). Polyphenolics were determined by a revised Folin–Denis method (King and Heath, 1967). The properties of the leaf and litter samples are shown in Table 1.

2.4. Charge characterization

Some specifics of tropical soils reflect on the choice of the methodology to measure the CEC. The charge of SOM is pH-dependent and most tropical soils have a

Table 1
Biochemical composition of the leaf and litter material from the multipurpose trees in the selected plots in the Ibadan arboretum

Tree species	C (g kg^{-1})	N (g kg^{-1})	Polyph[a] (g kg^{-1})	Polyph/N	Lignin (g kg^{-1})	Lignin/N	Cellulose (g kg^{-1})
Leaves							
Afzelia	467 ± 5 [b]	38.2 ± 0.8	6.4 ± 0.6	0.17 ± 0.02	87 ± 3	2.3 ± 0.1	287 ± 14
Dactyladenia	457 ± 4	15.9 ± 0.3	67.0 ± 2.1	4.21 ± 0.13	195 ± 14	12.2 ± 1.1	238 ± 9
Gliricidia	453 ± 3	46.6 ± 0.7	22.8 ± 5.0	0.49 ± 0.11	53 ± 16	1.1 ± 0.4	196 ± 18
Gmelina	465 ± 2	29.1 ± 0.5	17.7 ± 1.8	0.61 ± 0.07	130 ± 19	4.5 ± 0.7	264 ± 43
Leucaena	455 ± 1	53.0 ± 0.2	85.4 ± 11.5	1.61 ± 0.21	51 ± 12	1.0 ± 0.2	126 ± 19
Pterocarpus	478 ± 2	33.3 ± 0.4	15.6 ± 2.5	0.47 ± 0.08	152 ± 6	4.6 ± 0.2	248 ± 19
Treculia	467 ± 3	21.9 ± 0.3	88.2 ± 7.8	4.03 ± 0.40	91 ± 9	4.1 ± 0.4	215 ± 15
Litter							
Afzelia	286 ± 39	14.1 ± 1.7	1.5 ± 0.3	0.11 ± 0.01	197 ± 23	14.3 ± 3.1	175 ± 39
Dactyladenia	313 ± 18	9.5 ± 1.2	3.2 ± 0.4	0.34 ± 0.04	201 ± 12	21.5 ± 3.1	232 ± 34
Gliricidia	280 ± 58	13.6 ± 3.0	2.2 ± 0.5	0.17 ± 0.03	193 ± 14	14.8 ± 3.2	168 ± 42
Gmelina	350 ± 37	13.2 ± 1.2	4.9 ± 0.5	0.37 ± 0.03	217 ± 7	16.5 ± 1.7	230 ± 57
Leucaena	333 ± 35	17.3 ± 1.7	2.7 ± 0.7	0.16 ± 0.04	244 ± 36	14.0 ± 0.8	221 ± 57
Pterocarpus	272 ± 60	10.3 ± 2.7	3.4 ± 0.7	0.33 ± 0.05	224 ± 17	23.0 ± 6.6	171 ± 34
Treculia	369 ± 47	11.9 ± 1.9	10.5 ± 3.9	0.86 ± 0.20	267 ± 37	22.5 ± 0.6	224 ± 26

[a] Polyph: polyphenolics.

[b] Average ± standard deviation of four replicates.

low nutrient status; therefore, a method which operates at low ionic strength and at soil pH is preferred (Gallez et al., 1976; Morais et al., 1976). To account for this, we used the silver thiourea (AgTU) method to measure CEC. This method relies on a very high selectivity of the surface for the silver thiourea complex and allows CEC measurements at low ionic strength (0.01 M) and at any desired pH value (Pleysier and Juo, 1980).

An unbuffered AgTU-solution (0.01 M Ag^+, 0.1 M TU) was used to measure the CEC and the base saturation of the whole soil at the prevailing soil pH. The CEC of whole soil samples and the fractions was also measured at different pH-levels on the same sample because of limited amounts of fractionated material available. Charge characterization was carried out only on the three smallest fractions (clay and fine and coarse silt) and the smallest organic fraction (O53). The contribution of the other fractions to the CEC of the soil is negligible (Oorts et al., 2000).

Subsamples were weighed (3.0 g for the whole soil samples, 0.1–0.6 g for the fractions) in a centrifuge tube and 15 ml 10^{-3} M NaOH was added to increase the pH. The pH was measured after 2 h of shaking (end over end). When the pH was still below 8, a few drops of 1 M NaOH were added and the tube was shaken again. If the pH was between 8 and 9, 15 ml of an unbuffered AgTU-solution (0.02 M Ag^+, 0.2 M TU) was added and the tubes were shaken overnight. Subsequently, the pH was measured, the samples were centrifuged (15 min, 3000 rpm), and a 1 ml subsample was taken from the clear supernatant for Ag^+-analysis. Then, a small, known amount (0.01–0.1 ml) of 1 M HNO_3 was added to the content of the centrifuge tube to acidify the samples a first time. After 4 h of shaking, pH was measured again, samples were centrifuged, and a second subsample was taken. This procedure was continued until pH 3 was reached. Analysis for Ag was done by atomic absorption spectrometry and CEC was calculated by difference. The whole procedure resulted for each sample in six CEC measurements between pH 3 and 7.

2.5. Data analysis

The CEC–pH relationships of the whole soil samples and the fractions were described by linear regression. Linear regressions were also used to describe the effect of the carbon content on the intercepts and slopes of this CEC–pH relationship and hence to calculate the CEC of SOM in the whole soil and the different fractions. Multiple regressions (first-order model with two independent variables: pH and carbon content) were used in describing the importance of the carbon content on the CEC of the whole soil and the fractions. The effect of the biochemical composition of leaves and litter samples on the CEC of SOM was described using a multiple regression (first-order model with two independent variables: pH and a parameter describing the plant material) after normalization of the CEC for the carbon content of the whole soil or fractions. All data were analyzed with the general linear models procedure (proc GLM) of the SAS system (SAS, 1985).

3. Results and discussion

3.1. Whole soil samples

The soils in the arboretum were sandy with, on average, 79% sand, 13% silt, and 8% clay (Table 2).

Table 2
Soil characteristics of the surface (0–10 cm) horizons of the selected plots in the Ibadan arboretum

Treatment	C ($g\,kg^{-1}$)	N ($g\,kg^{-1}$)	pH	CEC ($cmol_c\,kg^{-1}$)	Sand[a] ($g\,kg^{-1}$)	Silt ($g\,kg^{-1}$)	Clay ($g\,kg^{-1}$)
Afzelia	7.68 ± 0.87[b]	0.51 ± 0.08	6.3 ± 0.2	3.79 ± 0.30	817 ± 10	113 ± 9	58 ± 4
Dactyladenia	12.04 ± 2.26	0.75 ± 0.15	5.5 ± 0.2	4.51 ± 0.78	779 ± 21	127 ± 11	78 ± 10
Gliricidia	7.48 ± 0.61	0.61 ± 0.08	5.5 ± 0.1	3.03 ± 0.57	811 ± 19	112 ± 5	68 ± 17
Gmelina	7.97 ± 0.41	0.66 ± 0.06	6.1 ± 0.2	3.90 ± 0.52	785 ± 9	120 ± 7	71 ± 7
Leucaena	13.62 ± 1.92	1.26 ± 0.19	6.0 ± 0.1	6.47 ± 0.87	738 ± 29	138 ± 9	107 ± 22
Pterocarpus	7.16 ± 0.77	0.52 ± 0.07	5.5 ± 0.2	2.80 ± 0.44	797 ± 17	116 ± 3	79 ± 14
Treculia	10.79 ± 1.29	0.62 ± 0.07	5.8 ± 0.1	5.08 ± 0.84	798 ± 26	122 ± 7	68 ± 18

[a] Sand: 0.053–2 mm; silt: 0.002–0.053 mm; clay: <0.002 mm.

[b] Average ± standard deviation of four replicates.

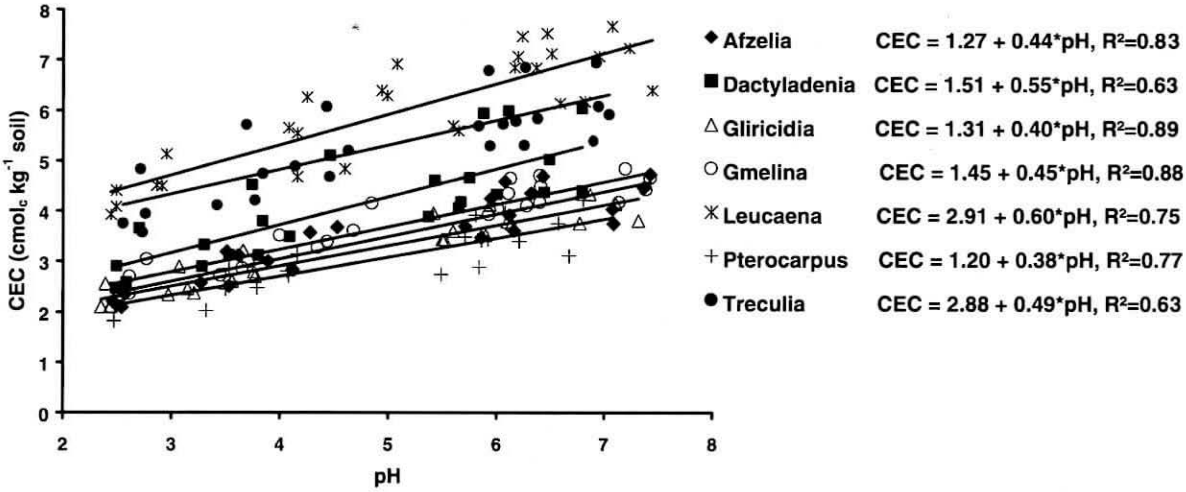

Fig. 1. CEC in function of pH for the different plots ($n = 24$, all regressions significant at $P = 0.001$).

Differences in texture between treatments were small. Soils with inputs from *Dactyladenia*, *Leucaena*, and *Treculia* had the highest organic carbon content. The other soils all had comparable lower values. The soil under *Leucaena* had, by far, the highest nitrogen content, about twice the nitrogen content of the other soils.

The CEC of these soils, measured at the prevailing soil pH (between 5.5 and 6.3), ranged between 2.8 and 6.5 $\mathrm{cmol_c\,kg^{-1}}$ soil (Table 2). These values were typical for highly weathered soils, such as a Ferric Lixisol (Gallez et al., 1976). The carbon content of the soils explained 77% of this variation in CEC and the small differences in pH also explained an additional significant ($P = 0.01$) part of the variation:

$$\mathrm{CEC} = 0.15 + 0.43\mathrm{C}\ (\mathrm{g\,kg^{-1}}),$$
$$n = 28,\ R^2 = 0.77,\ P < 0.001 \qquad (1)$$

$$\mathrm{CEC} = -6.97 + 1.25\mathrm{pH} + 0.41\mathrm{C}\ (\mathrm{g\,kg^{-1}}),$$
$$n = 28,\ R^2 = 0.87,\ P < 0.001 \qquad (2)$$

Besides the carbon content, the clay content of the soils did not explain an additional significant part of the variation in CEC. This proved our assumption that differences in CEC in these soils were due to differences in SOM content. From Eq. (1), it followed that the CEC of SOM at pH 5.8 (=average pH) in these soils was 430 ± 50 $\mathrm{cmol_c\,kg^{-1}}$ C.

When the CEC was measured at different pH values between 3 and 7 (Fig. 1), pH explained only 35% of the total variation, again indicating the important differences between treatments. Carbon content and pH together explained 85% of the variation (Table 3). Therefore, it could be concluded that the amount of SOM in the soil was the main source of variation between treatments.

Table 3
Influence of carbon content and pH on the CEC (cmol$_c$ kg^{-1} soil or fraction)

Fraction	Regression coefficients			$R^{2\,a}$
	Intercept	pH	C ($\mathrm{g\,kg^{-1}}$)	
Whole soil	1.61 ± 0.28[b]	0.52 ± 0.05	–	0.354
	0.62 ± 0.27	–	0.37 ± 0.03	0.515
	−1.79 ± 0.20	0.50 ± 0.03	0.36 ± 0.02	0.849
Clay	10.40 ± 0.49	2.64 ± 0.09	–	0.831
	9.99 ± 2.89	–	0.40 ± 0.08	0.122
	−0.73 ± 0.95	2.58 ± 0.07	0.33 ± 0.03	0.914
Fine silt	8.59 ± 1.60	2.37 ± 0.32	–	0.242
	−2.82 ± 1.23	–	0.49 ± 0.03	0.684
	−14.75 ± 0.65	2.47 ± 0.09	0.50 ± 0.01	0.947
Coarse silt	6.23 ± 1.03	1.18 ± 0.19	–	0.180
	−0.24 ± 0.58	–	0.41 ± 0.02	0.755
	−5.20 ± 0.50	1.05 ± 0.07	0.40 ± 0.01	0.898

[a] $n = 168$, all regressions significant at $P = 0.001$.
[b] Estimate ± standard error of estimate.

Table 4
Regressions between the intercepts and slopes of the CEC–pH relationships of the whole soil and the fractions and their carbon content

Fraction	Intercept		Slope		CEC SOM ($\mathrm{cmol_c\,kg^{-1}\,C}$)
	Equation	$R^{2\,a}$	Equation	R^2	
Whole soil	−0.05 + 0.194C	0.550	0.15 + 0.034C	0.807	194 (± 34)[b] + 34 (± 3)pH
Clay	6.74 + 0.114C	0.125	1.08 + 0.043C	0.423	114 (± 59) + 43 (± 10)pH
Fine silt	−2.84 + 0.238C	0.746	−0.09 + 0.056C	0.931	238 (± 27) + 56 (± 3)pH
Coarse silt	−1.15 + 0.264C	0.796	0.25 + 0.027C	0.681	264 (± 26) + 27 (± 4)pH
O53	2.25 + 0.144C	0.652	1.41 + 0.024C	0.587	144 (± 20) + 24 (± 4)pH

[a] $n = 28$, all regressions significant ($P < 0.001$), except for the intercept of clay ($P = 0.065$).

[b] Estimate ± standard error of estimate.

A linear regression model fitted the CEC–pH relationships for the soil samples of the different treatments (Fig. 1). The regressions were all highly significant ($P < 0.001$). Both intercepts and slopes showed some variation over the treatments. Intercepts of these equations were an estimate for the CEC at pH 0, while the slopes were a measure for the variable (pH-dependent) charge of these soils. Regressions between these intercepts and slopes and the carbon contents of the soils were highly significant (Table 4). Again, the clay content did not explain an additional significant part of the variation.

The CEC of SOM could be deduced from these equations. The value of the coefficient for carbon in the intercept-equation is the increase in the estimated CEC at pH 0 ($\mathrm{cmol_c\,kg^{-1}}$ soil) for an increase of $1\,\mathrm{g\,C\,kg^{-1}}$ soil. Similarly, the value of the coefficient for carbon in the slope-equation is the increase in the variable charge ($\mathrm{cmol_c\,kg^{-1}}$ soil) for an increase of $1\,\mathrm{g\,C\,kg^{-1}}$ soil. Consequently, the average CEC of SOM in these soils was $194 + 34\,\mathrm{pH\,cmol_c\,kg^{-1}\,C}$. According to this equation, the CEC at pH 5.8 was $391\,\mathrm{cmol_c\,kg^{-1}\,C}$, which corresponded with the value calculated from Eq. (1). These results were generally higher than values found in literature. Asadu et al. (1997) found values for the CEC of SOM ranging from 160 to $280\,\mathrm{cmol_c\,kg^{-1}\,C}$ (pH 7) for a range of soils from sub-Saharan Africa, but Meyer et al. (1994) reported CEC values for SOM between 111 and $693\,\mathrm{cmol_c\,kg^{-1}\,C}$ (pH 7–8.1) for soils across North America.

3.2. Fractions

3.2.1. Distribution of carbon and nitrogen

The carbon and nitrogen contents for both silt fractions showed the same differences as for the whole soil samples (Table 5). *Dactyladenia*, *Leucaena*, and *Treculia* had the highest carbon contents, while *Leucaena* had the highest nitrogen contents. The carbon and nitrogen values of the clay fractions were almost

Table 5
Organic carbon and total nitrogen content of the particle size fractions of the surface (0–10 cm) horizons of the selected plots in the Ibadan arboretum

Treatment	Organic carbon ($\mathrm{g\,C\,kg^{-1}}$)			Total nitrogen ($\mathrm{g\,N\,kg^{-1}}$)		
	Coarse silt	Fine silt	Clay	Coarse silt	Fine silt	Clay
Afzelia	23.3 ± 6.9[a]	40.3 ± 5.5	37.1 ± 3.1	1.55 ± 0.57	3.59 ± 0.46	4.57 ± 0.45
Dactyladenia	28.1 ± 3.8	52.4 ± 6.9	36.5 ± 3.7	1.74 ± 0.46	4.09 ± 0.75	4.72 ± 0.43
Gliricidia	27.6 ± 2.2	36.2 ± 1.6	33.0 ± 2.3	1.81 ± 0.26	3.14 ± 0.15	4.18 ± 0.37
Gmelina	18.8 ± 1.2	37.8 ± 1.8	35.3 ± 5.3	1.25 ± 0.13	3.66 ± 0.20	4.52 ± 0.74
Leucaena	42.0 ± 8.5	56.3 ± 7.3	35.7 ± 5.6	3.43 ± 0.81	5.77 ± 0.66	4.82 ± 0.86
Pterocarpus	24.0 ± 4.6	34.1 ± 4.7	29.4 ± 3.1	1.24 ± 0.26	2.85 ± 0.34	3.72 ± 0.48
Treculia	46.1 ± 5.0	65.8 ± 5.2	34.7 ± 5.3	2.07 ± 0.25	4.09 ± 0.17	4.45 ± 0.78

[a] Average ± standard deviation of four replicates.

constant for the different plots (29.4–37.1 g C kg^{-1} clay and 3.72–4.82 g N kg^{-1} clay).

For all the treatments, the fine silt fractions had the highest carbon contents of the fractions smaller than 0.053 mm, while the coarse silt fractions had the lowest. When the abundance of the fractions was taken into account, the fine silt fraction had the largest contribution to the carbon content of the whole soil (36–49% of the total amount of C). The clay fraction contributed 21–34%, the coarse silt fraction 9–18%, and the organic fractions in total 12–17%. The recovery of carbon in the fractions ranged from 87 to 102% of the amount found for the whole soil.

The nitrogen contents increased with decreasing particle size: clay > fine silt > coarse silt, except for the *Leucaena* plot where the fine silt fraction had the highest nitrogen content. Clay (40–53%) and fine silt fraction (39–54%) made the same contribution to the nitrogen content of the whole soil. The coarse silt fraction contributed only 7–14% and the organic fractions 9–16%. The nitrogen recovery in these five fractions varied from 107 to 130%. No sufficient explanation could be forwarded for these high recoveries.

3.2.2. Cation exchange capacity

As for the whole soil samples, a linear regression model fitted the CEC–pH relationships for all the fractions (Fig. 2). The regressions were all significant at $P < 0.01$ for the clay and fine silt fractions and at $P < 0.05$ for the coarse silt and organic fractions. The organic fraction (O53) had the highest CEC in $cmol_c\,kg^{-1}$ fraction for all treatments. The CEC varied between 20 and 60 $cmol_c\,kg^{-1}$ at pH 3, and between 40 and 90 $cmol_c\,kg^{-1}$ at pH 6. In spite of this

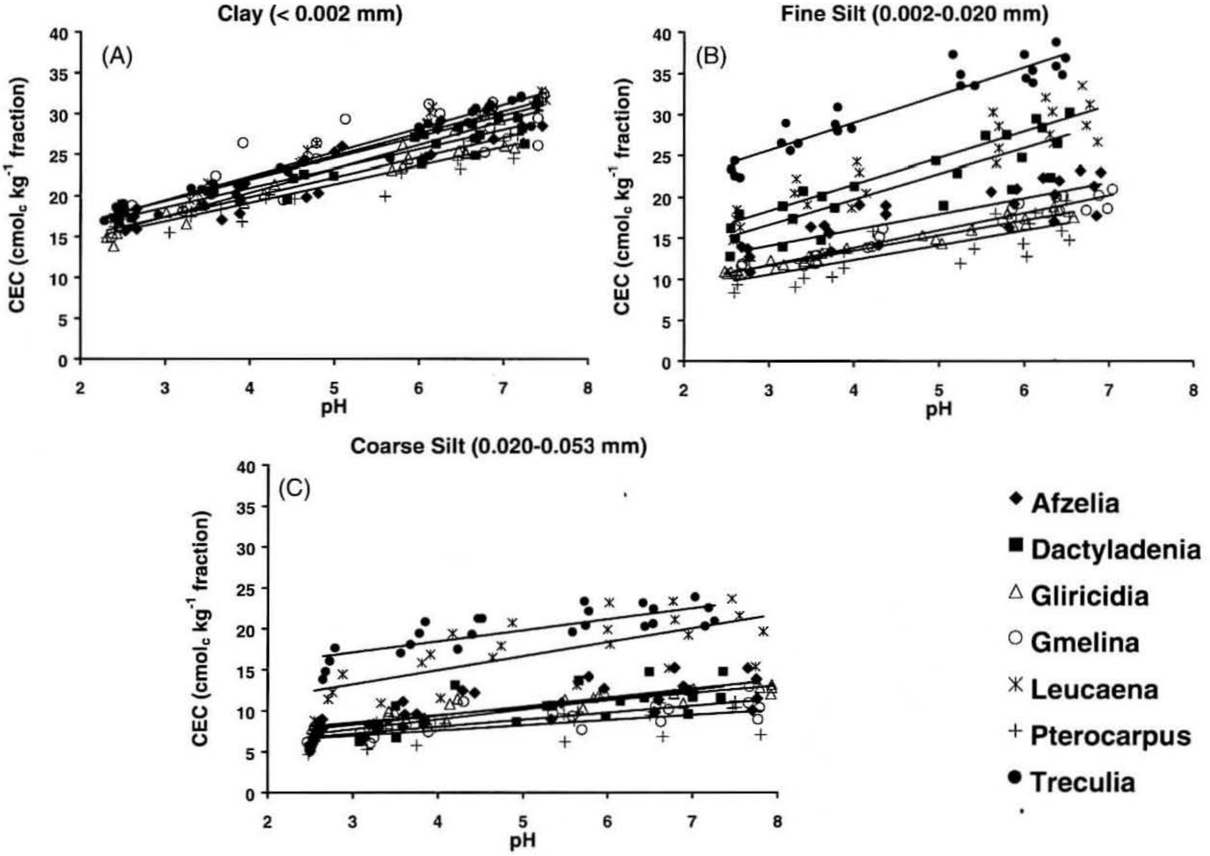

Fig. 2. CEC in function of pH for: (A) the clay fractions, (B) the fine silt fractions and (C) the coarse silt fractions of the different plots ($n = 24$, all regressions significant at $P = 0.01$ for clay and fine silt fractions and at $P = 0.05$ for the coarse silt fraction).

high CEC in $\mathrm{cmol_c\,kg^{-1}}$ fraction, the organic fractions had a low contribution (5–7% at pH 5.8) to the overall CEC because of their low abundance in the soil (3.2–6.9 $\mathrm{g\,kg^{-1}}$ soil).

The CEC of the coarse silt, fine silt, and clay fractions increased with decreasing particle size (clay > fine silt > coarse silt), except for *Treculia*, where the fine silt fraction had the highest CEC, and for *Dactyladenia* and *Leucaena*, where clay and the fine silt had comparable CEC values. Clay and the fine silt fraction had the highest contribution to the CEC of the whole soil; together they were responsible for 76–90% of the CEC of the soil at pH 5.8 (Fig. 3). The contribution of the fine silt fraction to the CEC at pH 5.8 ranged from 35 to 50%. For the soils under *Treculia* and *Dactyladenia*, this fine silt fraction had the highest contribution, while for the soils under *Afzelia* and *Leucaena*, clay and fine silt had a comparable contribution to the overall CEC. For the soils under *Gliricidia*, *Gmelina*, and *Pterocarpus*, the clay fraction was the main contributor to the CEC. The coarse silt fraction contributed 9–15% of the CEC. The recovery of the CEC in the fractions ranged from 95 to 104%. These results stressed the importance of the fine silt fraction for the physicochemical properties of the soil. Asadu et al. (1997) also reported the important contribution of the fine silt fraction to the CEC of sub-Saharan soils.

There was not much variation in the CEC of the clay fractions among the treatments (Fig. 2). The CEC varied between 15 and 20 $\mathrm{cmol_c\,kg^{-1}}$ fraction at pH 3, and 24 and 32 $\mathrm{cmol_c\,kg^{-1}}$ fraction at pH 7. The pH explained 83% of the variation (Table 3). The carbon content explained only a small additional part of the variation (8%). It is possible that the relatively high proportion of the CEC originating from the mineral components in this fraction may have obscured differences in CEC due to differences in organic matter content. However, because of the distribution pattern of carbon and nitrogen in the clay fractions, it was concluded that no important differences occurred between the treatments regarding the contribution of SOM to the CEC of this fraction.

For both silt fractions, more variation was observed between the treatments. For the fine silt fraction, pH alone explained only 24% of the variation, while carbon content and pH together explained 95%. The same was observed for the coarse silt fraction: pH alone explained 18% of the variation and carbon content and pH together 90%. This emphasized the importance of the carbon content in determining the CEC in these fractions and hence in the whole soil.

For each fraction, intercepts and slopes of the fitted CEC–pH relationships showed some variation over the treatments and were related with the carbon contents

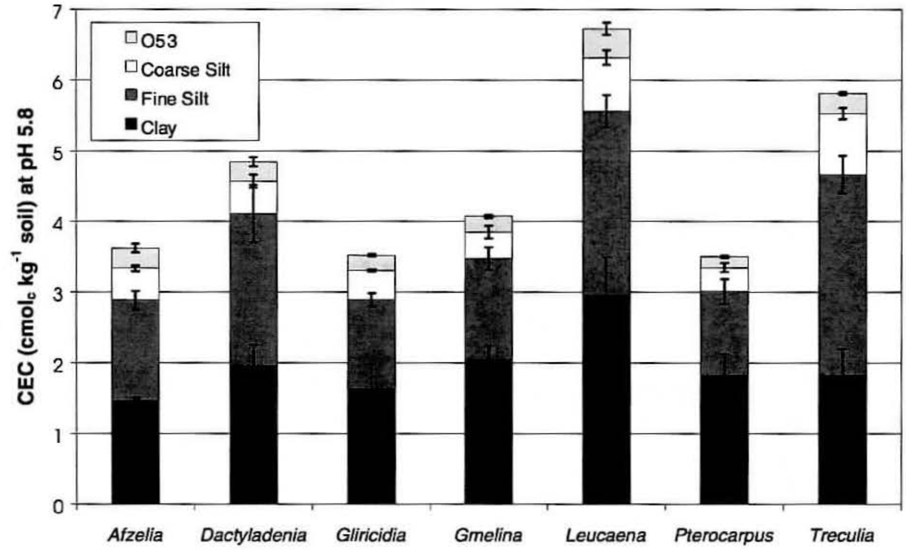

Fig. 3. Contribution of the different fractions to the CEC at pH 5.8 (error bars: ± standard deviation of four replicates).

(Table 4). The weakest relationships were found for the clay fraction. This agreed with the results from the multiple regressions between CEC ($\mathrm{cmol_c\,kg^{-1}}$ fraction) and pH and carbon content, and was due to the high contribution of the clay minerals to the CEC. The permanent and variable charge of these clay minerals could be deduced from the equations as being the estimated CEC at pH 0 and the pH-dependent charge at the absence of SOM ($C = 0\,\mathrm{g\,kg^{-1}}$):

$$\mathrm{CEC\ (cmol_c\,kg^{-1}\ clay)} = 6.74 + 1.08\,\mathrm{pH} \qquad (3)$$

This agreed with data on the CEC of kaolinitic clays found in literature (Weaver and Pollard, 1973). Intercepts of both the relationships between intercepts and slopes with carbon content were not significantly ($P = 0.01$) different from zero for both silt fractions and O53. Therefore it could be concluded that the inorganic particles in these fractions had a negligible CEC and that only SOM contributed to the CEC in these fractions. When the carbon contents in the clay fraction and the CEC of the clay and clay-sized SOM were taken into account, the contribution of SOM to the CEC of the clay fraction and hence of the whole soil samples could be calculated. SOM was responsible for 75% (*Pterocarpus*) to 85% (*Treculia*) of the CEC of these soils.

3.2.3. The CEC of soil organic matter

The estimated CEC at pH 0 and the pH-dependent charge of SOM in the different fractions could be calculated from the equations in Table 4. SOM in the fine silt fraction had the highest CEC (563 $\mathrm{cmol_c\,kg^{-1}}$ C at pH 5.8), followed by SOM in the coarse silt fraction (421 $\mathrm{cmol_c\,kg^{-1}}$ C at pH 5.8). The organic fraction had the lowest CEC: 283 $\mathrm{cmol_c\,kg^{-1}}$ C at pH 5.8. Clay-sized SOM had an intermediate CEC (363 $\mathrm{cmol_c\,kg^{-1}}$ C at pH 5.8), but care should be taken with this value: because of the weak regression for the intercept of the clay fraction, the estimate of this parameter was not very accurate. Except for this clay fraction, the CEC of SOM increased with decreasing particle size. This could be explained by the higher specific surface from the smaller fractions. Our results agreed with the findings of Thompson et al. (1989) who found an average value of 559 $\mathrm{cmol_c\,kg^{-1}}$ C at pH 7 for SOM in clay and silt fractions. Leinweber et al. (1993) reported CEC values between 280 and 600 $\mathrm{cmol_c\,kg^{-1}}$ C at pH 8.1 for SOM in particle size fractions.

3.2.4. Effect of the biochemical composition of organic inputs on the CEC of SOM

In order to determine any differences in the CEC of SOM between treatments, the CEC was normalized for the amount of carbon and expressed in $\mathrm{cmol_c\,g^{-1}}$ C. Except for the coarse silt fraction, pH alone explained more than 75% of the remaining variation in CEC when expressed in $\mathrm{cmol_c\,g^{-1}}$ C (Table 6). The biochemical composition of the leaf samples did not explain a substantial additional part of the remaining variation. The properties of the litter samples explained some more variation, but this was still very low (Table 6). Therefore, it was concluded that the effect of the biochemical composition of the organic inputs on the CEC of SOM was negligible. This did not agree with earlier results for the same soils (Oorts et al., 2000). An explanation for this disagreement was the difference in dispersion method between both studies. In the first study, soils were dispersed using sodium carbonate, which could have caused some important artefacts in the obtained fractions. Although, in that study, no carbonate was detected in the fractions, it appeared later that the clay fraction was strongly enriched with carbon after dispersion with sodium carbonate. This extra carbon could have been remaining carbonate or organic carbon from the dissolution of SOM due to the high pH (>10) during the dispersion. In particular, the possibility of the dissolution of organic components during dispersion could have led to artefacts related to the biochemical composition of SOM. The high pH of the obtained fractions could also have had an effect on the CEC measurement through precipitation of Ag_2S, although this was not observed. In order to avoid any possible artefact from the use of chemicals, ultrasonic dispersion was preferred in the present study. Therefore, the results shown here were thought to be more reliable.

Despite not showing any important direct effect on the CEC of the whole soil or fractions, the biochemical composition of the organic inputs has an important indirect effect through its influence on the decomposition rate and hence on the amount of carbon in the soil (Tian et al., 1992; Vanlauwe et al., 1996). For our data, the carbon content of the whole soil and fractions was

Table 6

Effect of the biochemical properties of the litter material on the CEC ($\mathrm{cmol_c\,g^{-1}\,C}$) of the whole soil and the fractions

Second parameter	Extra variation explained (%)	Regression equation[a]	R^2
Whole soil ($n = 172$)			
–	–	$\mathrm{CEC} = 0.174 + 0.053\,\mathrm{pH}$	0.7571
Polyphenolics	5.1	$\mathrm{CEC} = 0.148 + 0.053\,\mathrm{pH} + 0.0071\,\mathrm{polyphenolics}$	0.8079
Lignin	4.4	$\mathrm{CEC} = 0.039 + 0.053\,\mathrm{pH} + 0.0006\,\mathrm{lignin}$	0.8010
Clay ($n = 168$)			
–	–	$\mathrm{CEC} = 0.320 + 0.074\,\mathrm{pH}$	0.7919
Lignin	4.3	$\mathrm{CEC} = 0.113 + 0.074\,\mathrm{pH} + 0.0009\,\mathrm{lignin}$	0.8348
Fine silt ($n = 168$)			
–	–	$\mathrm{CEC} = 0.172 + 0.053\,\mathrm{pH}$	0.8753
Polyphenolics	4.9	$\mathrm{CEC} = 0.147 + 0.054\,\mathrm{pH} + 0.0061\,\mathrm{polyphenolics}$	0.9247
Coarse silt ($n = 168$)			
–	–	$\mathrm{CEC} = 0.218 + 0.038\,\mathrm{pH}$	0.5348
(Lignin + Polyph)/N[b]	9.7	$\mathrm{CEC} = 0.293 + 0.035\,\mathrm{pH} - 0.0040(\mathrm{lignin} + \mathrm{Polyph})/\mathrm{N}$	0.6315
Cellulose	8.7	$\mathrm{CEC} = 0.251 + 0.037\,\mathrm{pH} - 0.00027\,\mathrm{cellulose}$	0.6215

[a] All regressions significant at $P = 0.001$, only the best regressions are shown.

[b] Polyph: polyphenolics.

best correlated with the concentrations of polyphenolics (positive correlations, $P < 0.001$) and cellulose (negative correlations, $P < 0.001$) in the leaves. As the amount of litterfall and therefore the amount of organic inputs were not constant for the different plots, we assumed that the biochemical composition of the inputs even overruled the amount of organic inputs in determining the final SOM content. However, from this data it was not possible to draw direct conclusions on the effect of biochemical composition on the amount of SOM.

4. Conclusions

For all treatments, POM fractions had the highest CEC, expressed on a dry matter basis. The CEC of the coarse silt, fine silt and clay fractions increased with decreasing particle size: clay > fine silt > coarse silt, except for *T. africana*, where the fine silt fraction had the highest CEC, and for *D. barteri* and *L. leucocephala*, where clay and fine silt had comparable CEC values. The clay and fine silt fractions were responsible for 76–90% of soil CEC at pH 5.8. The contribution of the fine silt fraction to the CEC at pH 5.8 ranged from 35% for *G. sepium* and *P. santalinoides* to 50% for *T. africana*. This indicated the importance of this fraction for the properties of the whole soil. After 20 years of different organic inputs, this fine silt fraction showed most differences between these treatments. The clay fraction still seemed to be unaffected by the different organic inputs as it did not show clear differences in carbon and nitrogen content and CEC between the treatments. Consequently, the silt fractions determined the differences between the whole soil samples.

As carbon content and pH together explained more than 85% of the variation in CEC of all fractions and the whole soil, differences between treatments in the amount of carbon were responsible for the differences in CEC. Except for the estimated CEC at pH 0 of the clay fraction, SOM had a significant ($P < 0.001$) contribution to both the CEC at pH 0 and the pH-dependent charge of the whole soil and the fractions. Only in the clay fraction was there a significant contribution of the inorganic particles to the CEC. SOM was responsible for 75–85% of the CEC of these soils.

From the relationships between the intercepts and slopes of the fitted CEC–pH relationships and carbon content, the CEC of SOM could be calculated for the different fractions. The estimated CEC at pH 0 of SOM varied between 114 and 264 $\mathrm{cmol_c\,kg^{-1}\,C}$ and the pH-dependent charge varied between 24 and 56 $\mathrm{cmol_c\,kg^{-1}\,C}$. SOM in fine silt fractions had the highest CEC, while POM (0.053–0.250 mm) had the lowest. The effect of the biochemical composition of the organic inputs on the CEC of SOM was negligible.

Acknowledgements

K. Oorts acknowledges a grant as Research Assistant of the Fund for Scientific Research—Flanders (Belgium). This is IITA manuscript number IITA/01/CP/12.

References

Asadu, C.L.A., Diels, J., Vanlauwe, B., 1997. A comparison of the contribution of clay, silt, and organic matter to the effective CEC of soils of sub-Saharan Africa. Soil Sci. 162, 785–794.

Christensen, B.T., 1992. Physical fractionation of soil and organic matter in primary particle size and density separates. Adv. Soil Sci. 20, 1–90.

Duxbury, J.M., Smith, M.S., Doran, J.W., Jordan, C., Szott, L., Vance, E., 1989. Soil organic matter as a source and a sink of plant nutrients. In: Coleman, D.C., Oades, J.M., Uehara, G. (Eds.), Dynamics of Soil Organic Matter in Tropical Ecosystems. University of Hawaii Press, Honolulu, HI, pp. 33–67.

Gallez, A., Juo, A.S.R., Herbillon, A.J., Moormann, F.R., 1975. Clay mineralogy of selected soils in southern Nigeria. Soil Sci. Soc. Am. Proc. 39, 577–585.

Gallez, A., Juo, A.S.R., Herbillon, A.J., 1976. Surface and charge characteristics of selected soils in the tropics. Soil Sci. Soc. Am. J. 40, 601–608.

Gee, G.W., Bauder, J.W., 1986. Particle-size analysis. In: Klute, A. (Ed.), Methods of Soil Analysis, Part 1, 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI, pp. 383–411.

Kang, B.T., Akinnifesi, F.K., 1994. Performance of selected woody agroforestry species grown on an Alfisol and an Ultisol in the humid lowland of West Africa, and their effects on soil properties. J. Trop. For. Sci. 7, 303–312.

King, H.G., Heath, G.W., 1967. The chemical analysis of small samples of leaf material and the relationship between the disappearance and composition of leaves. Pedobiologia 7, 192–197.

Leinweber, P., Reuter, G., Brozio, K., 1993. Cation exchange capacities of organo-mineral particle-size fractions in soils from long-term experiments. J. Soil Sci. 44, 111–119.

Meyer, W.L., Marsh, M., Arp, P.A., 1994. Cation exchange capacities of upland soils in eastern Canada. Can. J. Soil Sci. 74, 393–408.

Morais, F.I., Page, A.L., Lund, L.J., 1976. The effect of pH, salt concentration, and nature of electrolytes on the charge characteristics of Brazilian tropical soils. Soil Sci. Soc. Am. J. 40, 521–527.

Oades, J.M., Gillman, G.P., Uehara, G., Hue, N.V., van Noordwijk, M., Robertson, G.P., Wada, K., 1989. Interactions of soil organic matter and variable-charge clays. In: Coleman, D.C., Oades, J.M., Uehara, G. (Eds.), Dynamics of Soil Organic Matter in Tropical Ecosystems. University of Hawaii Press, Honolulu, HI, pp. 69–95.

Oorts, K., Vanlauwe, B., Cofie, O.O., Sanginga, N., Merckx, R., 2000. Charge characteristics of soil organic matter fractions in a Ferric Lixisol under some multipurpose trees. Agrofor. Syst. 48, 169–188.

Pleysier, J.L., Juo, A.S.R., 1980. A single-extraction method using silver-thiourea for measuring exchangeable cations and effective CEC in soils with variable charges. Soil Sci. 129, 205–211.

SAS, 1985. SAS User's Guide: Statistics, 5th ed. SAS Institute, Cary, NC.

Thompson, M.L., Zhang, H., Kazemi, M., Sandor, J.A., 1989. Contribution of organic matter to cation exchange capacity and specific surface area of fractionated soil materials. Soil Sci. 148, 250–257.

Tian, G., Kang, B.T., Brussaard, L., 1992. Biological effects of plant residues with contrasting chemical compositions under humid tropical conditions—decomposition and nutrient release. Soil Biol. Biochem. 24, 1051–1060.

Van Dijk, H., 1971. Colloid chemical properties of humic matter. In: McLaren, A.D., Skujins, J. (Eds.), Soil Biochemistry, vol. 2. Marcel Dekker, New York, pp. 16–35.

Van Soest, P.J., 1963. Use of detergents in the analysis of fibrous feeds. II. A rapid method for determination of fiber and lignin. J. Assoc. Off. Anal. Chem. 46, 829–835.

Van Soest, P.J., Wine, R.H., 1967. Use of detergents in the analysis of fibrous feeds. IV. Determination of plant cell wall constituents. J. Assoc. Off. Anal. Chem. 50, 50–55.

Vanlauwe, B., Nwoke, O.C., Sanginga, N., Merckx, R., 1996. Impact of residue quality on the C and N mineralization of leaf and root residues of three agroforestry species. Plant Soil 183, 221–231.

Weaver, C.E., Pollard, L.D., 1973. The chemistry of clay minerals. Developments in Sedimentology, vol. 15. Elsevier, New York, 213 pp.