

Increasing negative charge and nutrient contents of a highly weathered soil using basalt and rice husk to promote cocoa growth under field conditions

Markus Anda^{a,*}, J. Shamshuddin^b, C.I. Fauziah^b

^a Indonesian Center for Agricultural Land Resource Research and Development, Agency of Agricultural Research and Development, Jalan Tentara Pelajar No. 12, Cimanggu Bogor 16114, Jawa Barat, Indonesia

^b Department of Land Management, Faculty of Agriculture, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

ARTICLE INFO

Article history:

Received 14 January 2013

Received in revised form 13 April 2013

Accepted 24 April 2013

Keywords:

Basalt

Rice husk

Surface charge

Oxisols

Cocoa

ABSTRACT

Technology intervention is a key success to restore properties and productivities of a highly weathered soil (Oxisols). The main challenge is to find materials with the ability to generate soil negative charge, release various nutrients and suppress toxic elements. The objective of this study was to increase negative charge and nutrient content, and suppress Al and Mn toxicities of an Oxisol using finely ground basalt and rice husk compost (RHC) to promote cocoa growth under field conditions. Factorial field experiment of 4×4 used finely ground basalt and rice husk compost and arranged in a randomly complete block design and planted to cocoa as a test crop. Finely ground basalt and rice husk compost were incorporated to the soil at 0–20 cm depth and rates varied from 0 to 20 t ha^{-1} each. Soils were periodically sampled for 24 months for analyses of soil negative charge, organic C content, various cations, pH and toxic elements. Results showed the rice husk compost (RHC) application significantly increased soil organic C content. The solid state cross polarization magic angle spinning ^{13}C carbon nuclear magnetic resonance (CP/MAS ^{13}C NMR) indicates RHC application was able to increase soil organic C functional groups (O-alkyl, di-O-alkyl and carboxyl C), accompanied by the appearance of aromatic, alkyl and methoxyl C as new functional groups. The carboxyl C plays a major role in generating soil negative charge, suggesting RHC is suitable to restore organic C and negative charge of Oxisols. Basalt, RHC and their combination were able to increase markedly the negative charge of Oxisols as revealed by the decreases in pH_0 and point zero net charge (PZNC) values. The decrease in pH_0 and PZNC values resulted in the increase of net negative charge of an Oxisol from 0.8 (a control soil) to 2.8, 4.1 and $5.0 \text{ cmol}_c \text{ kg}^{-1}$ for basalt, RHC and their combinations, respectively. *In situ* soil solution study (a new technique) under field conditions showed basalt and RHC applications either singly or in combination significantly increased the concentrations of Ca, Mg, K, Na and Si, while concentrations of toxic Al and Mn significantly reduced below a toxic level. Overall improvement of Oxisol chemical properties attributed by basalt and RHC applications significantly increased cocoa growth as revealed by the increase in height and stem diameter of cocoa which are two to three times faster than the control within a 24-month period.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Oxisols, highly weathered soils, are unproductive soils owing to advanced stage of development. According to von Uexkull and Mutert (1995), Oxisols occupied 727 million ha (18.4%) of the total world's acid soils (3950 million ha). In Malaysia, the Oxisols have little capacity to retain cations because of very limited negative charge under natural conditions. Anda et al. (2008a) reported that the Malaysian Oxisol (Segamat series) at natural conditions has heavy clay (79–81%), very low cation exchange capacity (CEC) ($<3.2 \text{ cmol}_c \text{ kg}^{-1}$) and cation contents (sum of

cations $<0.40 \text{ cmol}_c \text{ kg}^{-1}$) but has high Al saturation (77–83%) within the upper two soil horizons.

It appears that Oxisols strongly need intervention of technology to increase their negative surface charge, replenish their nutrient loss and alleviate Al and Mn toxicities. By using technology, the natural basalt could be processed as a potential material to generate soil negative charge, increase soil pH and released most of the essential cations (Gillman et al., 2002; Anda et al., 2009), thereby it offers a good insight to solve the problems of a highly weathered soil such as Oxisols.

In soils, the negative charge derived from inorganic functional groups (hydroxyl of Si, Al and Fe) and organic functional groups (enolic, phenolic and carboxyl) (Charlet and Sposito, 1987; Duquette and Hendershot, 1993). The intrinsic charge of soil particles consisted of permanent charge and variable charge

* Corresponding author. Tel.: +62 02518323012; fax: +62 02518311256.
E-mail address: markusandas@yahoo.com (M. Anda).

components (Sposito, 1989; Chorover et al., 2004). According to Gillman (2007) permanent charge (negative or positive) is the structural charge resulted from isomorphous substitution during crystal formation and the magnitude is not altered by the change in the pH or ionic strength of the surrounding solution. In contrast, the variable charge (negative or positive) is the charge that develops on (principally) surface hydroxyl groups by protonation and deprotonation reactions. The magnitude of the variable charge is dependent on pH and ionic strength of surrounding solution.

Oxisols have lost ability to retain base cations owing to low or limited amount of negative charge, low pH and high Al content, which collectively became major limiting factors for crop growth. Hence, the key success in using Oxisols for agricultural practices mainly relies on technology intervention to manipulate their existing constraint chemical properties and lack of nutrients. Manipulation of chemical properties and increasing nutrient content of highly weathered soils using finely ground basalt have been carried out under laboratory conditions (Gillman et al., 2002; Anda, 2006) and glasshouse conditions (Anda et al., 2009). Results from both laboratory and glasshouse conditions showed that application of finely ground basalt on Oxisols (highly weathered soils) were able to increase negative charge (cation exchange capacity), exchangeable cations and suppress Al and Mn contents. The improvement of soil properties has significantly improved cocoa growth under glasshouse conditions (Anda et al., 2009). However, environmental factors, especially temperature and soil moisture regimes, are fully controlled under laboratory and glasshouse conditions. These factors are difficult to control under field conditions, therefore, the field experiment is needed to observe the ability of basalt in increasing soil negative charge and improving cocoa growth. Since basalt dissolution took place under the condition that sufficient soil moisture content (field capacity) or during a rainy season, attempts should be made (e.g. compost application) to increase soil water contents under field conditions, thereby more basalt dissolution. Hence, the experiment was designed using basalt and organic matter applications under field conditions to restore properties and nutrient content of a highly weathered soil to support optimal crop growth. It is expected that the field experiment could show similar results to basalt applications under laboratory and glasshouse conditions.

Rice husk distributed in the rice mills as the main by-product and agro-waste that cause serious environmental problems (Kapur, 1985). It is being produced in more than 75 countries around the world (Natarajan et al., 1998) and the annual world output is about 116 million tons (FAO, 2002). Although rice husk was quite resistant to microbial decomposition due to its high cellulose and lignin contents (Anda et al., 2008b), it could provide special benefit to crops when used as a soil ameliorant. This beneficial effect is related to prolonged residual effect, which was really needed in tropical conditions due to rapid decomposition of organic matter as a result of being exposed to high temperature and rainfall. It has been confirmed that rice husk compost has a

long resident time in soil and hence it is a good source of SOM (Anda et al., 2010). Currently, no information is available for applying rice husk for upland soils in association with cocoa growth. The objective of this study was to increase negative charge and nutrient content, and suppress Al and Mn toxicities of a highly weathered soil using finely ground basalt and rice husk compost (RHC) to promote cocoa growth under field conditions.

2. Materials and methods

2.1. Location and materials

The field experiment was carried out at the Malaysian Cocoa Board (MCB) Experimental Station in Jengka, Pahang, Malaysia. The site selected was former forest and had been cleared for the extension of the cocoa research area by MCB. The soil is classified as a fine clayey, kaolinitic, isohyperthermic, Rhodic Hapludox (Soil Survey Staff, 2010). Mineralogical composition of the clay fraction of the soil studied had been reported by Anda et al. (2008a), where kaolinite was dominant (83%) followed by goethite (10%) and hematite (5%). The area had been planted with *Gliricidia sepium* as preparation to shade the young cocoa. Rice husk compost was bought from the private company. The basalt was supplied by Pacific Mineral Developments Pty Ltd, Australia, in the form of finely ground basalt rock. The particle sizes were $\leq 50 \mu\text{m}$ (53%), 50–106 μm (26%), 105–250 μm (14%), 250–500 μm (5%) and 500–2000 μm (2%). In the present study, the particle size of $\leq 250 \mu\text{m}$ was used. Major chemical compositions obtained from X-ray fluorescence (XRF) analyses provided by the company were CaO (8.97%), MgO (10.70%), K₂O (1.79%), Na₂O (2.59%), SiO₂ (43.20%), Al₂O₃ (12.90%), Fe₂O₃ (12.90%), P₂O₅ (0.77%), and SO₂ (<0.01%).

The cocoa seedlings were prepared as top-budding using the collection seedling of MCB as the root stock and that the KKM22 and PBC 123 cultivars as the top-plant. After top-budding, the seedlings were grown in the nursery for 6 months and then selected to obtain the relatively uniform growth to be transplanted to the experimental plots.

The average annual rainfall at the station is 1887 mm with 165 rain days. The wet season (monthly rainfall >200 mm) occurs from October to December, the moist seasons (monthly rainfall 100–200 mm) occur from March to May and from July to September, and the dry seasons (monthly rainfall <100 mm) occur in January, February, and June. The amount of annual evaporation is much lower (42 mm) than the annual rainfall, so there is always sufficient soil moisture. The annual minimum (20–23 °C) and maximum (30–33 °C) temperatures are relatively constant throughout the year, with an average of 26–28 °C. Some relevant soil properties prior to field trial of the studied Oxisol is given in Table 1. The soil pH was strongly acid, very limited amounts of exchangeable cations (<0.4 cmol_c kg⁻¹), low organic matter content and high Al saturation in the topsoil (77–83%).

Table 1
Selected physical and chemical properties of the Oxisol studied.

Horizon	Depth (cm)	Particle size (%)			C (%)	N (%)	pH		Al (cmol _c kg ⁻¹)	Exchangeable (cmol _c kg ⁻¹)		cation	Sum cat. (cmol _c kg ⁻¹)	CEC pH 7 (cmol _c kg ⁻¹)	Al sat. (%)
		Clay	Silt	Sand			H ₂ O	KCl		Ca	Mg	K	Na		
A	0–14	79	17	3	1.4	0.13	4.19	4.00	1.41	0.15	0.23	0.02	nd	0.41	77
Bo1	14–45	81	15	3	1.0	0.10	4.27	4.08	1.12	0.09	0.11	0.02	nd	0.23	83
Bo2	45–85	82	15	3	0.9	0.08	4.25	4.36	0.38	0.09	0.14	0.02	nd	0.24	61
Bo3	85–117	81	16	3	0.8	0.07	4.49	4.57	0.16	0.08	0.19	0.02	nd	0.29	35
Bo4	117–165	84	13	3	0.8	0.05	4.58	4.58	0.16	0.10	0.08	0.02	nd	0.20	44

Adapted from Anda et al. (2008a).

nd, not detected; Sum cat., sum of cations; Al sat, Al saturation.

2.2. Methods

The application rates of basalt were 0, 5, 10 and 20 t ha⁻¹, designated as B0, B1, B2 and B3, respectively. The rates of rice husk compost (RHC) were 0, 5, 10 and 20 t ha⁻¹, designated as R0, R1, R2 and R3, respectively. The highest rate of 20 t ha⁻¹ for basalt and RHC was selected because it was the optimal rate obtained from glasshouse experiments. The study was set up as a 4 × 4 factorial experiment with three replications and arranged in a randomized complete block design (RCBD). Each plot size was 9 m × 9 m. The basalt was applied one month prior to transplanting to promote basalt reaction with soils, whereas the rice husk compost (RHC) was applied at the time of transplanting. Basalt and RHC were manually incorporated into 0–20 cm soil depth. Each plot had 3 rows and 9 cocoa seedlings were grown in rows with spacing of 3 m × 3 m. The center row was grown with KKM 22 cultivar and the isle rows with PBC 123 cultivar. The mixture of two cultivars instead of single cultivar in a given plot was preferred in order to allow the cross pollination, resulting more pods and yields compared to single cultivar (personal communication with Mr. Nik Aziz Nik Mat, Head of experimental station). Basal fertilizers were N and K and applied as urea (1 g seedling⁻¹) and KCl (1 g seedling⁻¹) forms. This was applied by diluting in distilled water at the time of planting and after 4 months. NPK green (15:15:15) was applied at 50 g seedling⁻¹ at 10 months after planting. Three plants KKM 22 were observed for each plot and the average was used to represent each replicate treatment.

Soil samples of about 150 g were taken from the center row at 0–15 cm depth, 40 cm from planting point (composite of 12 sampling points), for every three months using a small stainless steel auger for a 24-month period. The soils were air-dried, ground and passed through a 2 mm sieve and kept for total C, pH, organic C functional groups, pH₀ and point zero net charge (PZNC) analyses.

In situ soil solution study as a new technique for field study was performed to observe types of ions release from basalt and RHC into solution and was considered ready to be absorbed by plants. It was sampled at month 24 using soil moisture samplers under wet soil conditions. This sampler consisted of a hydrophilic, porous polymer and a connector for attaching a vacuum syringe (10 ml) to extract soil solution. The aliquot was used for electrical conductivity measurement using conductivity meter and pH measurement using pH meter (Thermo Orion, Model 410a). The Ca, Mg, K, Na, Si, Fe, Al and Mn were determined using an inductively-coupled plasma emission spectrometry (ICPES).

Total organic C was determined by a combustion technique using a CR-412 carbon analyzer (LECO, Corporation, St. Joseph, USA). One g soil was weighed into a tared ceramic boat and pushed into the furnace of carbon analyzer. The sample was then ignited in a stream of oxygen at 1350°C and the amount of CO₂ released was measured by an infra red detector. After calibration against a standard using CaCO₃ (12.0% C), the instrument printed the total C result in %.

The parameter used to assess charge characteristics of variable charge component is pH₀, while for the whole charge (variable and permanent charges) is point zero net charge (PZNC). According to Gillman (2007) pH₀ is the point of zero charge of all of the variable charge soil components. At this pH, there are equal numbers of protonated and deprotonated sites, and hence equal amounts of negative and positive variable charge. PZNC is the point of zero net charge of the whole soil. At this pH there are equal amounts of negative and positive charge, irrespective of the origin of charge, and hence total cation exchange capacity (CEC_T) is equal anion exchange capacity (AEC) at PZNC.

Determination of pH₀ was carried out as described by Gillman and Sumner (1987). Six portions of 2 g 2-mm air-dried samples were weighed into 50 mL centrifuge tubes and saturated with

0.1 M CaCl₂, and subsequently washed and equilibrated with 0.002 M CaCl₂, which was considered equivalent to the ionic strength of natural soil solution. Using HCl or Ca(OH)₂, the pH of the suspension was adjusted to six values in the range from 3.5 to 6.5. When equilibrium occurred for 0.002 M CaCl₂, the pH was recorded as pH_{0.002} and then 0.5 mL of 2 M CaCl₂ was added and the pH was again recorded as pH_{0.05} after equilibration. The position of pH₀ was obtained from the zero difference between pH_{0.05} and pH_{0.002} by interpolation.

Point of zero net charge (PZNC) was determined from pH value where equal amounts of index cation and anion were adsorbed. The negative charge (referred to as CEC) and positive charge (referred to as AEC) were determined as described by Gillman (1984) except that the amounts of Ca²⁺, Al³⁺ and Ca²⁺ plus Al³⁺ adsorbed were referred to as base cation exchange capacity (CEC_B), acidic cation exchange capacity (CEC_A) and total cation exchange capacity (CEC_T), respectively (Gillman and Sumpter, 1986). The sum of Al and Ca adsorbed, representing total negative charge in the electrical double layer. The amount of Ca adsorbed represented a portion of negative charge occupied by exchangeable cations. This measurement was referred to charge measurement under equilibrium soil pH values, which were span from pH 2.5 to 5.0. In addition, another set of charge measurement was carried out at soil pH for individual basalt rate, i.e., without equilibration over pH ranges. Measurements of CEC_B, CEC_A, CEC_T and AEC at soil pH would closely represent charge generation under natural field condition after basalt application.

Chemistry of rice husk compost was determined using solid state cross polarization magic angle spinning ¹³C carbon nuclear magnetic resonance (CP/MAS ¹³C NMR) and their spectra were obtained using a Bruker Avance 400 spectrometer (Faellanden, Switzerland). The sample was packed into a zircon rotor with diameter of 4 mm. The spectrometer was operated at a ¹³C frequency of 100.62 MHz with a spinning speed of 5 kHz at the magic angle of 54.7° to the magnetic field, contact time of 1 ms, and recycle delay of 5 s. For each spectrum, 15,000 scans were recorded and the chemical shifts were referenced externally to tetramethylsilane (TMS). The ¹³C NMR spectra were divided into eight regions (Inbar et al., 1989; Baldock and Skjemstad, 2000; Marche et al., 2003). Region I (0–45 ppm) is assigned to alkyl C or carbons that are bonded only to other carbons; region II (45–65 ppm) is assigned to N-alkyl and methoxyl C (C–N, C–O bonds); region III (65–95 ppm) is assigned to O-alkyl C; region IV (95–110 ppm) represents di-O-alkyl carbon groups; region V (110–145 ppm) represents aromatic and unsaturated C; region VI (145–160 ppm) represents phenolic C; region VII (160–190 ppm) represents amide and carboxyl C; region VIII (190–220 ppm) represents aldehyde and ketone C. The region 0–60 ppm was partitioned as aliphatic C, 60–110 ppm as polysaccharide C and 110–160 ppm as aromatic C. The area of each peak was calculated as the peak height times the width at half height (Wershaw et al., 1996). The relative intensity of these regions was determined by the integration of the corresponding peak areas. The functional groups of phenolic C and carboxyl C were responsible for generating negative charge in soils.

Agronomic observation included cocoa height and diameter, measured every 3 months. The cocoa height was measured from the soil surface, whereas the diameter was at 5 cm from the soil surface.

3. Results and discussion

3.1. Effect of rice husk compost and basalt on soil organic C

Changes of soil organic C during a 24-month period showed application of RHC significantly increased SOC, while basalt

Table 2

The effect of rice husk compost and basalt applications on total soil organic C at different sampling times over a 24-month period.

RHC rate	Basalt rate (%)				Average (%)
	B0	B1	B2	B3	
Month 3					
R0	1.66d	1.93b	1.87c	2.22a	1.92d
R1	2.23c	2.11b	2.40b	2.45a	2.30c
R2	2.75b	2.77a	2.42b	2.37a	2.58b
R3	3.31a	2.90a	3.13a	2.57a	2.97a
Average	2.49A	2.43A	2.45A	2.40A	
Month 6					
R0	1.48c	1.81b	1.75c	2.18a	1.81b
R1	1.80c	1.88b	2.23b	2.04a	1.99b
R2	2.23ab	2.24ab	2.37b	2.26a	2.28a
R3	2.46a	2.59a	2.60a	2.14a	2.45a
Average	2.00A	2.13A	2.24A	2.15A	
Month 9					
R0	1.37b	1.64b	1.59b	1.85a	1.61a
R1	1.61b	1.74ab	1.93a	2.00a	1.82a
R2	2.03a	2.16a	1.79ab	1.85a	1.96a
R3	2.13a	1.91ab	2.02a	1.73a	1.95a
Average	1.79A	1.86A	1.83A	1.86A	
Month 12					
R0	1.32c	1.60a	1.44b	1.70a	1.51b
R1	1.56b	1.58a	1.88a	1.83a	1.71a
R2	1.82a	1.96a	1.61ab	1.76a	1.79a
R3	2.02a	1.77a	1.84a	1.65a	1.82a
Average	1.68A	1.73A	1.69A	1.74A	
Month 15					
R0	1.29b	1.61ab	1.57c	1.75a	1.56b
R1	1.66ab	1.57b	1.88ab	2.07a	1.79a
R2	2.01a	2.06a	1.70bc	1.80a	1.89a
R3	2.03a	1.88ab	1.96a	1.67a	1.88a
Average	1.75A	1.78A	1.78A	1.82A	
Month 18					
R0	1.63c	1.90a	1.75a	2.00a	1.82b
R1	1.90b	1.88a	2.15a	2.23a	2.04ab
R2	2.25a	1.99a	1.83a	1.93a	2.00ab
R3	2.45a	2.10a	2.19a	1.80a	2.14a
Average	2.06A	1.97A	1.98A	1.99A	
Month 24					
R0	1.74c	2.10a	1.91a	2.14a	1.97b
R1	2.05bc	1.94a	2.29a	2.42a	2.17ab
R2	2.49ab	2.34a	2.16a	2.24a	2.31a
R3	2.58a	2.30a	2.32a	2.10a	2.33a
Average	2.22A	2.17A	2.17A	2.22A	

Note: Numbers within each column followed by a similar small letter or within each row followed by a similar capital letter are not significantly different at 5% probability level. R, rice husk; B, basalt; R0, R1, R2 and R3 or B0, B1, B2 and B3 are 0, 5, 10 and 20 t ha⁻¹, respectively.

application had no effect on SOC (Table 2). Every rate of RHC application (all R with B0) significantly increased SOC content for the first three months. The following 6, 9, 12, 15, 18 and 24 months, only application rates at 10 and 20 t ha⁻¹ significantly increased SOC, suggesting the significant residual effect of RHC application was less than 6 months for 5 t ha⁻¹ rate and at least 24 months for 10 and 20 t ha⁻¹ rates under field conditions.

Furthermore, the correlation was made between total SOC and duration of RHC application to predict the decrease in SOC with time. The trend showed soil organic C content consistently decreased with increasing time of application for the first 12 months (Fig. 1). Surprisingly, there is an increase in total SOC with time from months 15 to 24. An attempt was made to predict SOC loss by regressing SOC and time for the first 12 months (figure not shown). The result indicated a negative linear relationship between SOC and duration of application periods. From linear equation of correlations, it was predicted that SOC losses were

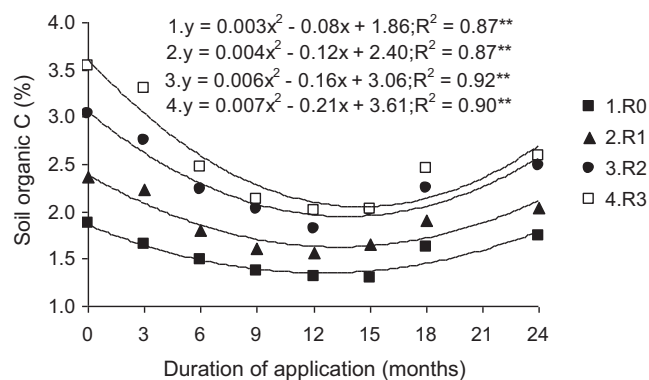


Fig. 1. Relationship between total soil organic C and duration of rice husk compost application.

0.05, 0.07, 0.11 and 0.14 unit per month for application rates at 0, 5, 10 and 20 t ha⁻¹, respectively under field conditions.

The increase in SOC at months 15–24 was attributed to the contribution from *Gliricidia sepium* litterfall. This shading plant produced significant amount of litter biomass and contributed to SOC. An attempt was made to partition SOC contributed by RHC alone by subtracting the organic C of the control treatment from each application rate. This attempt was unsuccessful because the result indicated the SOC content was still higher at months 15–24 compared to month 12 (data not shown). This indicates that there is an interaction between soil organic functional groups derived from RHC and *Gliricidia* to preserve SOC. This is an unexpected trend, but may provide a positive impact on soil organic matter management by mixing rice husk compost and *Gliricidia* as a means to preserve SOC.

3.2. Chemistry of soil organic C derived RHC

Sources of organic C under the field trial were RHC as a treatment and litterfall of *Gliricidia* as shade of young cocoa crops. According to Anda et al. (2010) the organic C structures of *Gliricidia* litter contained much higher alkyl C (35%) compared to alkyl C (10%) derived RHC. In addition, the proportion of O-alkyl C was much higher for RHC (58%) than *Gliricidia* litterfall (30%), while di-O-alkyl, aromatic, phenolic and carboxyl C were relatively similar between the two SOM sources.

The solid state CP/MAS ¹³C NMR showed the application of RHC increased the intensity of resonance peaks at 75 and 105 ppm, indicating the presence O-alkyl and di-O-alkyl C, respectively (Fig. 2). In addition, there new peaks appeared at 30, 125 and 153 ppm indicating alkyl, aromatic, and phenolic C, respectively. The calculation of each C structure by integration at month 6 showed O-alkyl, alkyl and aromatic C account for 47, 20 and 13%, respectively of the total signals. The magnitude of contribution from other C types is small (<8%) and are in the order of di-O-alkyl C > carboxyl > methoxyl > phenolic C. At month 12, major changes occurred as revealed by proportion change and signal disappearance of organic C types. O-alkyl C contribution to the signal decreased considerably from 47 to 36%, accompanied by disappearance of C types in alcohol and methoxyl regions. In addition, there were increases in the proportion of alkyl C (16–24%), aromatic and carboxyl C (13 and 16% each). These indicate the alkyl, aromatic and carboxyl C functional groups of RHC were selectively preserved in the soils. This trend is expected to continue to month 18. However, this is not the case, instead di-O-alkyl C increased and aromatic and carboxyl C decreased, whereas O-alkyl, alkyl and phenolic C were relatively unchanged. The unexpected increase in di-O-alkyl C at month 18 was due to the organic C input

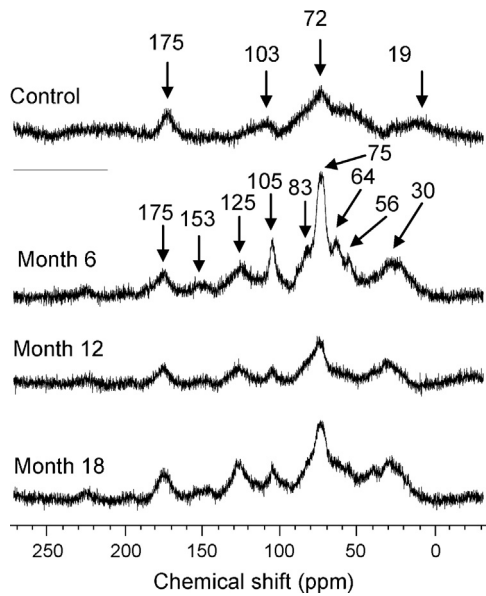


Fig. 2. The cross polarization magic angle spinning (CP/MAS) ^{13}C nuclear magnetic resonance (NMR) spectra of an Oxisol treated with rice husk compost at different sampling times after 18 months.

from *Gliricidia* litter that contained more easily decomposable carbohydrate such as di-O-alkyl C. Implication of RHC application to highly weathered soils is the increased SOC content and changes in soil organic chemistry to improve soil properties. The carboxyl and phenolic C or amino reactive groups of organic soil constituents are responsible for the generation of variable negative charge in the soil (Qafoku et al., 2004).

3.3. Effects of basalt and RHC on soil pH and charge properties

3.3.1. Soil pH

Basalt application increased soil pH values (varying from pH 4.0 to 5.3) with increasing basalt rates (Fig. 3). The trend of soil pH

increased from months 3 to 9 and then relatively constant at high values to month 24. The exception was soil pH values slightly decreased at month 12 in all cases (treated and untreated basalt soils). The reason for this is not understood. The soil pH is remain high to the end of field trial indicating that basalt has long residual effect in increasing soil pH. For rice husk compost (RHC) application, soil pH significantly increased from 4.0 to 5.2, depending on application rate. The soil pH values were still higher for the soil treated with RHC than the control treatment after 24 months suggesting a long residual effect on soil pH. The control soil showed the pH trend is slightly increased from months 6 to 24 probably due to the effect of soil organic matter derived from *gliricidia* litter (shading plant for young cocoa) to form complex with Al, which in turn reduced soil acidity. Combination of various basalt rates with R1 and R2 rates of RHC showed the increase in soil pH values was higher compared to any rate of basalt or RHC application alone (Fig. 3a and b vs c and d). This may reflect interaction of basalt and RHC in increasing pH of highly weathered soils. It is considered that RHC application has an ability to increase soil moisture regime, which promotes more dissolution of basalt leading to the increase of soil pH.

Results from glasshouse experiment (Anda et al., 2009) showed similar trend to field trial, where the soil pH increased with increasing rates of basalt application. However, the pH values for corresponding basalt application rates were higher for field conditions than glasshouse conditions. This is probably due to acidity from rainfall and organic matter (*gliricidia*) to accelerate dissolution of finely ground basalt under field conditions.

3.3.2. Point of zero charge

The application of rice husk compost (RHC) lowered pH_0 values and its magnitude continuously decreased with increasing duration of application periods (Fig. 4). The exception was pH_0 values slightly increased (0.2 unit) at a 20 t ha^{-1} rate for month 3 and 0.1 unit at 10 and 20 t ha^{-1} rates for month 6. This indicates the RHC begin to generate negative soil surface charge but slightly increase positive charge at high application rates ($>10 \text{ t ha}^{-1}$). However, all RHC rates decreased pH_0 from 3.8 to 3.4 for month 12 and from 3.7 to 3.0 for month 24. This indicates RHC application

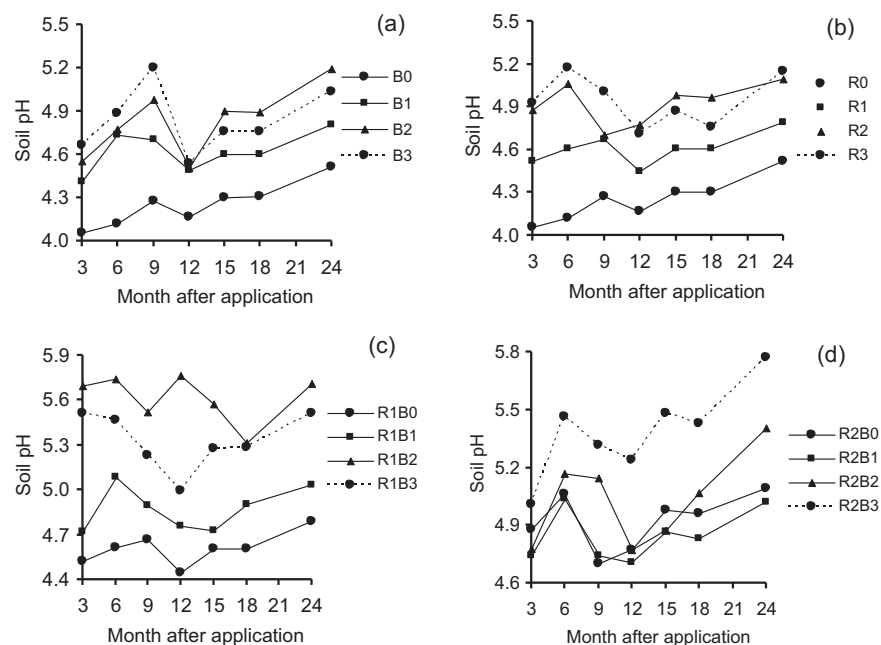


Fig. 3. Changes of soil pH values with time after basalt and RHC applications: (a) basalt application, (b) RHC application, (c) various basalt rates at R1 rate, and (d) various basalt rates at R2 rate.

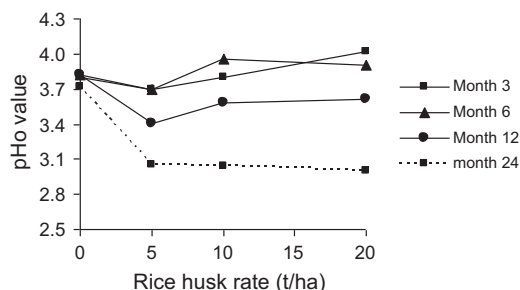


Fig. 4. Changes of pH_o values with time after RHC application.

needs a longer time to associate with soil particle surfaces to generate more soil negative charge. This is related to RHC mainly consists of cellulose which needs longer time to be decomposed by microorganisms.

The effect of basalt application on pH_o was measured after application of 12 and 24 months because glasshouse experiment indicated that the basalt rates considerably lowered pH_o values after 12 months (Anda et al., 2009). Under field conditions, the basalt application showed pH_o decreased from 3.8 to 3.5–3.7 for month 12 (Table 3). The pH_o values further decreased from 3.7 to 3.3–3.5 after month 24, indicating that basalt continuously decreased pH_o until the end of the experiment. This is related to silicate released from basalt experiencing hydrolysis to form silicic acid (H_4SiO_4), which in turn decreased pH_o value.

Furthermore, the combination of RHC and basalt lowered pH_o values (Table 3). The comparison of various combination rates to RHC or basalt application alone showed pH_o values were lower for combination of 20 t ha^{-1} RHC (R3) with any basalt rate than the basalt or RHC alone after 12 month application. Further increase in duration of application to two years indicated RHC rates of 10 and 20 t ha^{-1} in combination with basalt rates decreased pH_o from 3.7 to 3.2–3.4. These pH_o values were lower compared to corresponding combinations at month 12, suggesting that combination of basalt and RHC continuously increased negative charge of the Oxisol, which in turn increased soil capability to retain cations.

3.3.3. Point of zero net charge

The application of either RHC or basalt was able to decrease PZNC values. The RHC application decreased PZNC values from 3.5 to 2.7, while basalt from 3.5 to 3.1 after 24 months (Table 4). There was consistent decrease in PZNC values with increasing application rates of either rice husk or basalt alone for the rates less than 20 t ha^{-1} . For the 20 t ha^{-1} application rate (R3 or B3), the PZNC values were slightly higher than the lower application rates. The combination of basalt and RHC decreased PZNC but there is no

Table 4

The effect of basalt and RHC on PZNC and soil surface negative charge at natural soil pH after 24 month.

Basalt	RHC			
	R0	R1	R2	R3
PZNC				
B0	3.54	2.70	2.70	2.90
B1	3.35	3.00	3.30	2.70
B2	3.10	3.20	2.90	3.10
B3	3.40	2.80	2.70	3.20
CEC _B (%)				
B0	94.16	96.73	97.94	96.92
B1	95.95	97.93	96.87	97.15
B2	95.93	97.54	97.28	97.26
B3	97.69	98.03	97.78	96.97
CEC _A (%)				
B0	5.84	3.27	2.06	3.08
B1	4.05	2.07	3.13	2.85
B2	4.07	2.46	2.72	2.74
B3	2.31	1.97	2.22	3.03
CEC _T (cmol _c kg ⁻¹)				
B0	3.03	5.40	5.87	6.39
B1	4.39	5.43	5.61	5.80
B2	5.00	6.13	6.49	6.24
B3	5.43	6.49	7.06	6.72
N _{et} C (cmol _c kg ⁻¹)				
B0	-0.84	-3.03	-3.70	-4.10
B1	-2.05	-2.77	-2.90	-3.45
B2	-2.48	-3.59	-3.95	-4.14
B3	-2.77	-3.75	-4.97	-4.66

CEC_B, negative charge for basic cation (Ca adsorbed); CEC_A, negative charge for acidic cation (Al adsorbed); CEC_T, total negative charge (Ca + Al adsorbed); N_{et}C, net charge (positive charge – CEC_T). B, basalt; R, rice husk compost; R0, R1, R2 and R3 or B0, B1, B2 and B3 are 0, 5, 10 and 20 t ha^{-1} , respectively.

consistent different trend for any combination rates. In addition, the PZNC values of the combination were lower compared to basalt alone but were higher compared to RHC alone. This indicates basalt not only promote negative charge generation but also (to some extent) generates positive charge.

Measurement of base negative charge (CEC_B), at equilibrium pH spanned from about 2.5 to 5.0, showed the application of RHC or basalt increased CEC_B values with increasing pH values and that the magnitude was higher compared to the control (R0 or B0) (Fig. 5). The magnitude of negative charge was the highest at the high equilibrium pH value and RHC rate (20 t ha^{-1}), whereas application at 5 and 10 t ha^{-1} rates, the CEC_B was practically similar at all corresponding pH values. For basalt rates, the magnitude of increased CEC_B was similar for all rates at pH ≤ 4 but CEC_B increased with the increase in rates at pH 5 (Fig. 5c).

In contrast to the negative charge, the positive charge decreased with increasing equilibrium pH values for all RHC or basalt rates (Fig. 5b and d). Unexpectedly, the trend of RHC rates showed the magnitude of positive charge was in the order R0 > R3 > R2 > R1, indicating the lower rate is more effective in decreasing soil positive charge, but all RHC rates decreased positive charge compared to untreated soils (the control = R0). In all cases, however, the magnitude of negative charge exceeded the positive charge, resulting in a net negative charge. Unlike RHC, the trend of basalt rates was not consistent in decreasing soil positive charge with increasing basalt rate at any equilibrium pH values. Under natural soil pH, the Oxisol used in this study contains positive charge of 2.2 cmol_c kg⁻¹ (Fig. 6a). This positive charge is slightly higher than the amount of positive charge (varying from 0.2 to 1.9 cmol_c kg⁻¹) of subsoils of highly weathered soils from tropical and subtropical areas reported by Qafoku et al. (2000).

The combination of basalt and RHC rates showed consistent increase of negative charge with increasing equilibrium pH values

Table 3

The values of pH_o at months 12 and 24 after basalt and RHC applications.

Basalt	RHC			
	R0	R1	R2	R3
Month 12				
B0	3.82	3.62	3.58	3.61
B1	3.67	3.60	3.40	3.45
B2	3.51	3.32	3.45	3.40
B3	3.57	3.50	3.52	3.51
Month 24				
B0	3.72	3.05	3.04	3.00
B1	3.40	3.50	3.18	3.50
B2	3.31	3.55	3.30	3.30
B3	3.46	3.31	3.31	3.40

Note: R, rice husk compost; B, Basalt. R0, R1, R2 and R3 or B0, B1, B2 and B3 are 0, 5, 10 and 20 t ha^{-1} , respectively.

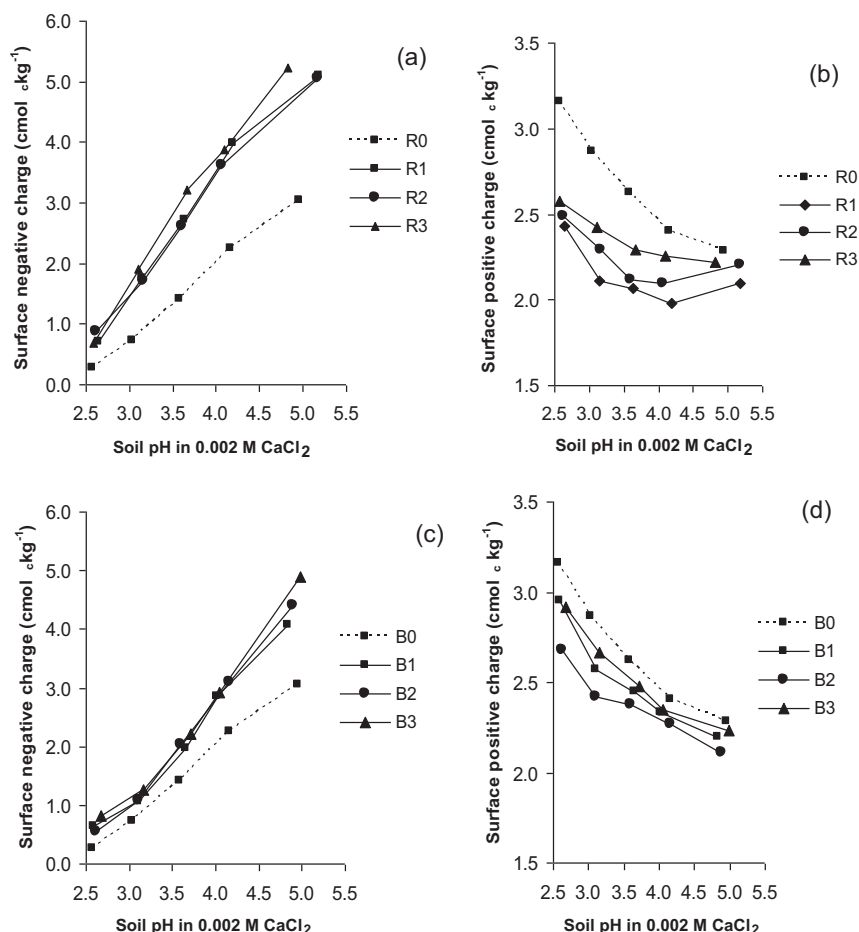


Fig. 5. Variation of surface charges at equilibrium pH values as affected by basalt or composted rice husk rates after 24-month application: (a) base-negative charge with rice husk treatments (R), (b) positive charge with rice husk treatments (R), (c) base-negative charge with basalt treatments (B), and (d) positive charge with basalt treatments (B). Note: B, basalt; R, rice husk compost; R0, R1, R2 and R3 or B0, B1, B2 and B3 are 0, 5, 10 and 20 t ha⁻¹, respectively.

(from 2.5 to 5.0) and the reverse is true for positive charge. In most cases, the high negative charge was shown by the highest basalt rate (B3 = 20 t ha⁻¹) in combination with any RHC rate (Fig. 5a). Except for R2B1 treatment, all combination rates decreased positive charge from 3.2 to 3.0–2.1 cmol_c kg⁻¹ at pH 2.5 and from 2.3 to 2.2–1.8 cmol_c kg⁻¹ at pH 5.0 (Fig. 5b). No consistent trend for the effect of combination of basalt and RHC rates on the magnitude of positive and negative charges.

To represent the effect of basalt, RHC and their combination on actual field conditions, the charge measurement was performed at natural soil pH values (without equilibration and changing pH) after 24 months of basalt and CRH applications (Fig. 6). The basalt or RHC application remarkably increased negative charge of the low negative charge Oxisol. The magnitude was higher for RHC than basalt at any corresponding rate application (Fig. 6a). The RHC increased negative charge from 2.9 to 6.2 cmol_c kg⁻¹ depending on application rate, whereas for basalt it increased from 2.9 to 4.9 cmol_c kg⁻¹. This indicates RHC application is faster than basalt in increasing negative charge of the Oxisol. In contrast to negative charge, the effect of RHC on positive charge of an Oxisol showed relatively constant values at different application rates, indicating RHC has no considerable amount of positive charge. For basalt application, there was a tendency to slightly increase the positive charge.

The effect of basalt and RHC combinations at natural pH showed the increase in surface negative charge (referred to as CEC_B) with increasing application rates (Fig. 6b) and their magnitude was

higher compared to either basalt or RHC alone. The combination increased negative charge from 2.9 to 6.9 cmol_c kg⁻¹, depending on combination rates. For the positive charge, it slightly increased with the increase in basalt rates in combination with RHC rates of 5 t ha⁻¹ (R1). However, basalt combination with high RHC rates showed no considerable change in surface positive charge values. It seems that basalt application to an Oxisol resulted much high amount of negative charge compared to positive charge on colloidal surfaces.

3.4. Effect of basalt and RHC on ions released into in situ soil solution

The application of RHC and basalt significantly increased Ca, Mg, Si, K and Na concentrations of the *in situ* soil solution, whereas concentrations of Al and Mn significantly decreased below the toxic level of crops (Table 5). The exception for Ca concentration, it increased with RHC application rates but was not statistically significant (Fig. 7). There is a significant effect of interaction between RHC and basalt applications in increasing Ca, Mg, Na and Si and in decreasing Mn. However, there was no effect of interaction on K and Al concentrations.

Concentrations of Ca, Mg, Si and K in soil solution significantly increased at RHC application rates of ≥10 t ha⁻¹, whereas the Na concentration only significantly increased at 20 t ha⁻¹ application. The dominant ions in soil solution were in the order of decreasing content Si > Ca > K > Mg > Na. The consistently increased concentrations of Ca, Mg, K, Na and Si with increasing RHC rates

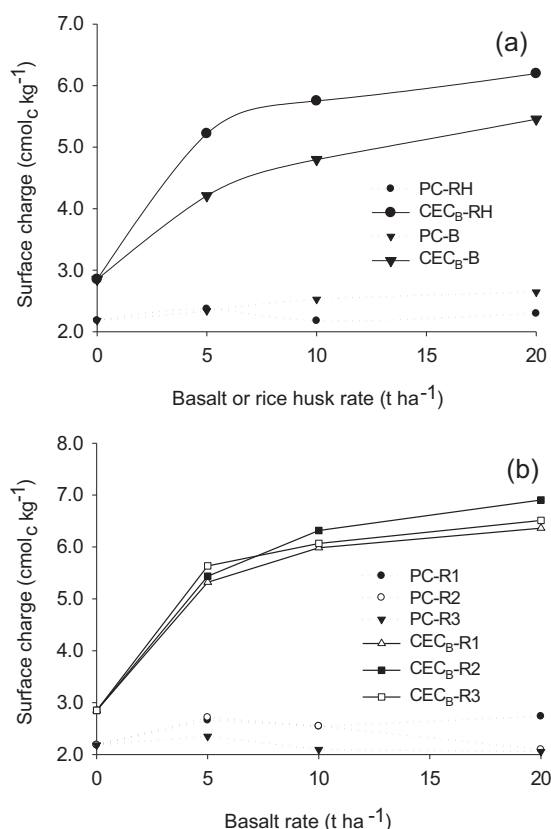


Fig. 6. The effect of basalt and composted rice husk on negative charge (CEC_b) and positive charge (PC) at natural soil pH after 24 months: (a) rice husk (R) or basalt (B) alone, and (b) combination of basalt and rice husk. Note: R1, R2 and R3 are 5, 10 and 20 $t\ ha^{-1}$, respectively.

suggested that RHC is a suitable amendment to supply plant nutrients for the Oxisol.

For basalt application, the concentrations of Ca, Mg and K significantly increased at 5 and 10 $t\ ha^{-1}$ and then decreased at

Table 5

Summary of statistical analysis for the effect of rice husk compost and basalt applications on various ions of *in situ* soil solution after a 24-month period.

Treatment	Ions						
	Ca	Mg	K	Na	Si	Al	Mn
Rice husk (RHC)	ns	***	*	***	**	***	**
Basalt (B)	**	***	*	***	***	***	***
RHC \times B	*	***	ns	***	***	ns	**

Note: ns, $P > 0.05$.

* $P < 0.05$.

** $P < 0.01$.

*** $P < 0.0001$.

20 $t\ ha^{-1}$. The decrease in Ca, Mg and K concentrations at 20 $t\ ha^{-1}$ basalt application could be explained by three possibilities. First, Ca, Mg and K were preferentially absorbed by cocoa in order to satisfy the high amount needed and left behind small amount in solution. Secondly, low solubility of basalt as the soil moisture was not sufficient to dissolve basalt at high application rate. Thirdly, the application of basalt at high rate promotes amorphous formation, which in turn, reduced soil surface negative charge and consequently led to leaching of cations.

In addition, concentrations of Na (Fig. 7d) and Si (Fig. 8a) consistently increased with basalt rates. The interaction of RHC and basalt significantly increased Ca, Mg, Si and Na concentrations at the rates of 5–10 $t\ ha^{-1}$ but it decreased at 20 $t\ ha^{-1}$. For the Al concentration, it significantly decreased at $\geq 10\ t\ ha^{-1}$ basalt rates or at $\geq 5\ t\ ha^{-1}$ RHC rates (Fig. 8b). For Mn, its concentration significantly decreased at 20 $t\ ha^{-1}$ RHC in combination with 5 $t\ ha^{-1}$ basalt and at 5 $t\ ha^{-1}$ RHC in combination with 20 $t\ ha^{-1}$ basalt (Fig. 8c). In addition, basalt application reduced less Al and more Mn compared to RHC at similar rates of 10 and 20 $t\ ha^{-1}$. The combination of RHC of 20 $t\ ha^{-1}$ with any basalt rate reduced Al to the lowest level.

3.5. Effect of RHC and basalt application on cocoa growth

The application of RHC, basalt and their combination significantly increased the height and stem diameter of cocoa ($P < 0.05$)

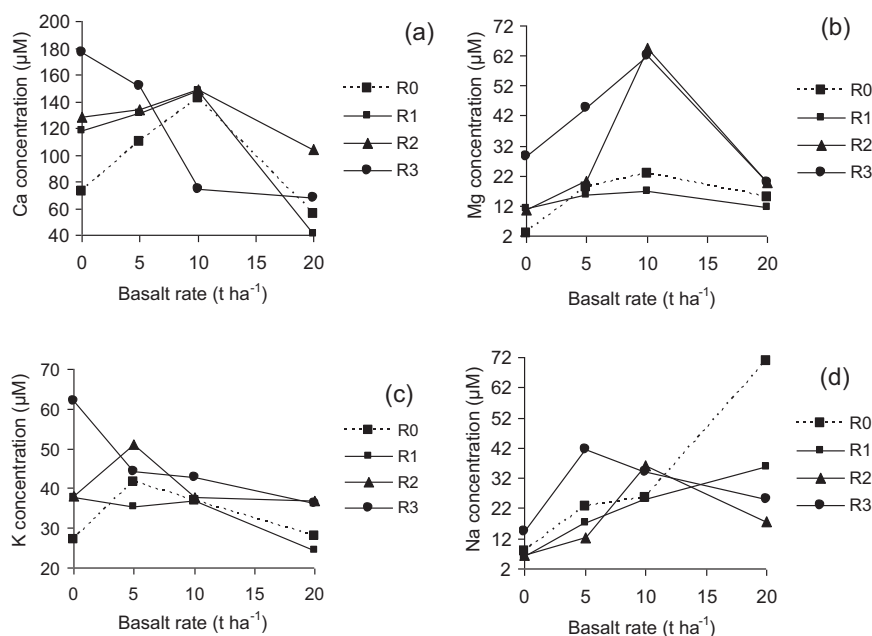


Fig. 7. The effect of RHC and basalt application on (a) Ca, (b) Mg, (c) K and (d) Na ion of *in situ* soil solution. Note: R0, R1, R2 and R3 are 0, 5, 10 and 20 $t\ ha^{-1}$, respectively.

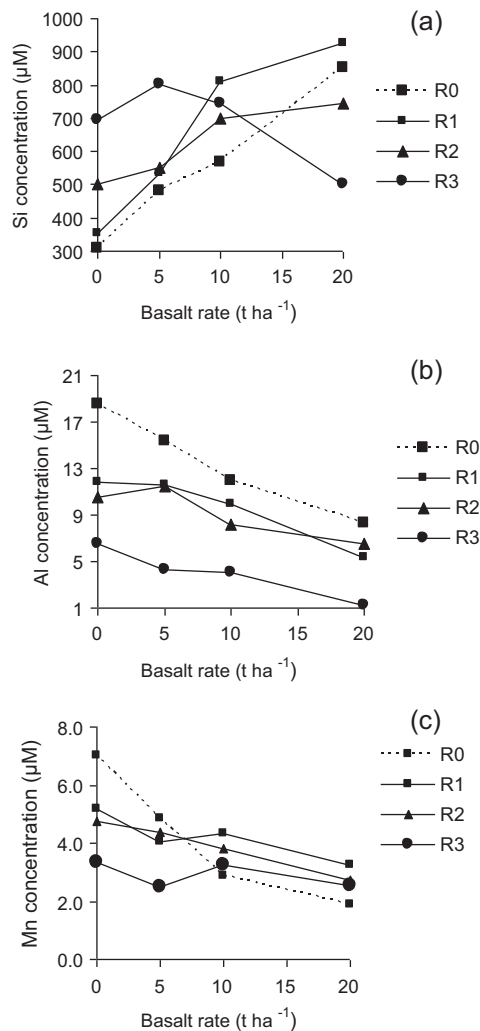


Fig. 8. The effect of RHC and basalt application on (a) Si, (b) Al, and (c) Mn ion of *in situ* soil solution. Note: R0, R1, R2 and R3 are 0, 5, 10 and 20 t ha^{-1} , respectively.

(Figs. 9 and 10). For basalt application alone, it significantly increased height and diameter of cocoa at 5 to 10 t ha^{-1} application rates after months 18 and 24, whereas other growing periods of less than 18 months showed no significant effect of basalt application (Figs. 9a and 10a). Application at a highest rate ($B_3 = 20 \text{ t ha}^{-1}$) showed no significant increase of cocoa height although the height was higher than the control. This indicates the high rate application needs long period of time to completely dissolved and reacted with soil in generating the favorable conditions for cocoa growth. The effect of basalt on cocoa growth was slower under field conditions compared to glasshouse conditions. Glasshouse experiment showed basalt application significantly increased cocoa growth (dry matter weight of cocoa) at 10 t ha^{-1} application rate after 15 months (Anda et al., 2009), while the corresponding rate occurred after 18 months under field conditions.

The application of RHC alone significantly increased height and diameter of cocoa for application rates of 5–20 t ha^{-1} compared to a control treatment and there were no further significant differences in height and diameter of cocoa at 5–20 t ha^{-1} rates (Figs. 9b and 10b). The significant increases in height and diameter of cocoa occurred at month 6 for a 20 t ha^{-1} rate, months 9 for a 10 t ha^{-1} and month 15 for 5 t ha^{-1} rates. This indicates the slow effect of RHC on cocoa growth at a low rate of application. Hence to obtain the rapid effect, RHC should be applied at high rates.

The effect of duration of applications (months 6, 9, 12, 15, 18 and 24) showed combination of basalt and RHC significantly increased height (Fig. 9c and d) and diameter (Fig. 10c and d) of cocoa with time. The combination of basalt and RHC at 5, 10 and 20 t ha^{-1} significantly increased cocoa height for every three month increment within a 24 month period. However, the non treated soil (control treatment) could only significantly increase height and diameter of cocoa after 9 months, followed by every 6 month increment within the period of 24 months. This indicated that basalt and RHC were able to promote cocoa height of two to three times faster than the control.

The application of 5 t ha^{-1} of either RHC or basalt alone significantly increased cocoa growth. The increased rates to

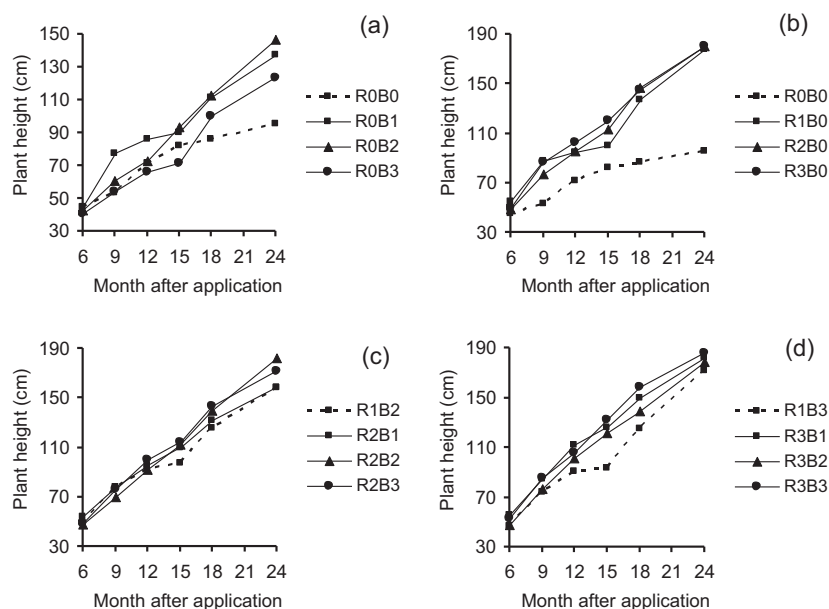


Fig. 9. Effect of basalt and RHC on height of cocoa over a 24-month period: (a) Basalt without RHC, (b) RHC without basalt, (c) Combination of R1 and R2 with basalt rates, and (d) Combination of R1 and R3 with basalt rates. Note: B, basalt; R, rice husk compost; R0, R1, R2 and R3 or B0, B1, B2 and B3 are 0, 5, 10 and 20 t ha^{-1} , respectively.

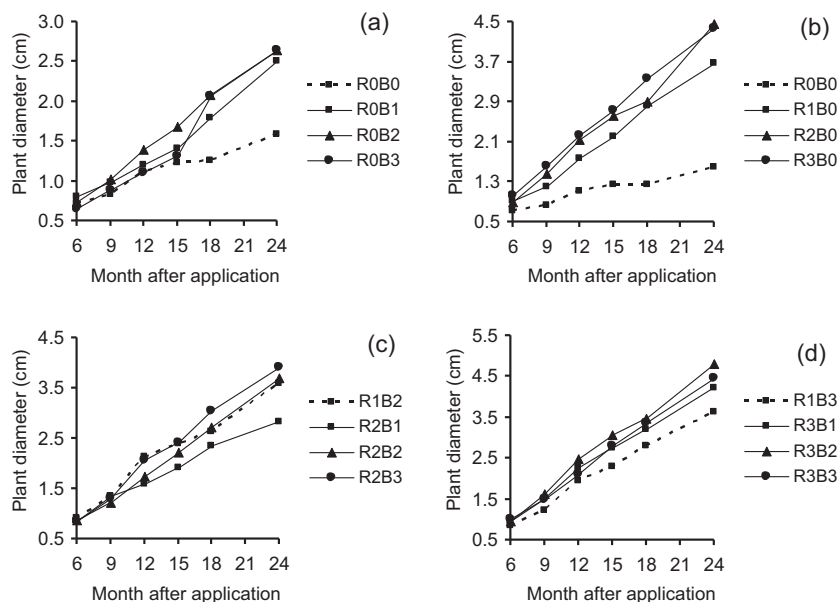


Fig. 10. Effect of basalt and RHC on diameter of cocoa over a 24-month period: (a) Basalt without RHC, (b) RHC without basalt, (c) Combination of R1 and R2 with basalt rates, and (d) Combination of R1 and R3 with basalt rates. Note: B, basalt; R, rice husk compost; R0, R1, R2 and R3 or B0, B1, B2 and B3 are 0, 5, 10 and 20 t ha⁻¹, respectively.

10 and 20 t ha⁻¹ showed no further significant increase in cocoa growth compared to 5 t ha⁻¹. Hence, for practical purpose, the rate of 5 t ha⁻¹ is suggested for either RHC or basalt application.

4. Conclusions

The rice husk compost (RHC) application significantly increased soil organic C content. The CP/MAS ¹³C NMR indicates RHC application was able to increase soil organic C functional groups (O-alkyl, di-O-alkyl and carboxyl C), accompanied by the appearance of aromatic, alkyl and methoxyl C as new functional groups. The carboxyl C plays a major role in generating soil negative charge.

Basalt, RHC and their combination decreased pH₀ from 3.7 to 3.3, 3.0 and 3.2, respectively. The corresponding values for PZNC decreased from 3.5 to 3.1, 2.7 and 2.7. These decreases in pH₀ and PZNC values have increased net negative charge of an Oxisol from 0.8 to 2.8, 4.1 and 5.0 cmol_c kg⁻¹ for basalt, RHC and their combinations, respectively.

The concentrations of Ca, Mg, K, Na and Si of *in situ* soil solution significantly increased for RHC application at 20 t ha⁻¹. The concentrations of these ions significantly increased for all basalt rates, except for Ca, Mg and K which decreased at 20 t ha⁻¹. Basalt, RHC and their combination significantly reduced toxic Al and Mn.

Application of basalt, RHC and their combination significantly increased cocoa growth as revealed by the increase in height and stem diameter of cocoa which are two to three times faster than the control within a 24 month period. The combination of RHC and basalt with the rate of 5 t ha⁻¹ each is suggested for practical application as this rate significantly increased cocoa growth compared to the control and was not significantly different to 10 and 20 t ha⁻¹ application rates.

References

Anda, M., 2006. Improvement of Charge Characteristics of Oxisols Using Basalt and Rice Husk Compost for Cocoa Growth. PhD thesis. Faculty of Agriculture. Universiti Putra Malaysia, Malaysia.

- Anda, M., Shamshuddin, J., Fauziah, C.I., Syed Omar, S.R., 2008a. Mineralogy and factors controlling charge development of three Oxisols developed from different parent materials. *Geoderma* 143, 153–167.
- Anda, M., Omar, S.S.R., Shamshuddin, J., Fauziah, C.I., 2008b. Changes in properties of composting rice husk and their effect on soil and cocoa growth. *Communications of Soil Science and Plant Analysis* 39, 2221–2249.
- Anda, M., Shamshuddin, J., Fauziah, C.I., Syed Omar, S.R., 2009. Dissolution of ground basalt and its effect on oxisol chemical properties and cocoa growth. *Soil Science* 174, 264–271.
- Anda, M., Shamshuddin, J., Fauziah, C.I., Syed Omar, S.R., 2010. Increasing the organic matter content of an Oxisol using rice husk compost: changes in decomposition and its chemistry. *Soil Science Society of America Journal* 74, 1167–1180.
- Baldock, J.A., Skjemstad, J.O., 2000. Role of soil matrix and minerals in protecting natural organic materials against biological attack. *Organic Geochemistry* 31, 697–710.
- Charlet, L., Sposito, G., 1987. Monovalent ion adsorption by an Oxisol. *Soil Science Society of America Journal* 51, 1155–1160.
- Chorover, J., Amistadi, M.K., Chadwick, O.A., 2004. Surface charge evolution of mineral-organic complexes during pedogenesis in Hawaiian basalt. *Geochimica et Cosmochimica Acta* 68, 4859–4876.
- Duquette, M., Hendershot, W.H., 1993. Soil surface charge evaluation by back-titration: I. Theory and method development. *Soil Science Society of America Journal* 57, 1222–1228.
- FAO, 2002. Statistical database. <http://apps.fao.org>. (accessed on 23.04.04).
- Gillman, G.P., 1984. Using variable charge characteristics to understand the exchangeable cation status of oxic soils. *Australian Journal of Soil Research* 22, 71–80.
- Gillman, G.P., Sumner, M.E., 1987. Surface charge characterization and soil solution composition of four soils from the Southern Piedmont in Georgia. *Soil Science Society of America Journal* 51, 589–594.
- Gillman, G.P., Sumpter, E.A., 1986. Surface charge characteristics and lime requirements of soils derived from basaltic, granitic, and metamorphic rocks in high rainfall tropical Queensland. *Australian Journal of Soil Research* 24, 173–192.
- Gillman, G.P., Burkett, D.C., Coventry, R.J., 2002. Amending highly weathered soils with finely ground basalt rock. *Applied Geochemistry* 17, 987–1001.
- Gillman, G.P., 2007. An analytical tool for understanding the properties and behavior of variable charge soils. *Australian Journal of Soil Research* 45, 83–90.
- Inbar, Y., Chen, Y., Hadar, Y., 1989. Solid-state carbon-13 nuclear magnetic resonance and infrared spectroscopy of composted organic matter. *Soil Science Society of America Journal* 53, 1695–1701.
- Kapur, P.C., 1985. Production of reactive bio-silica from the combustion of rice husk in a tube-in-basket (TiB) burner. *Powder Technology* 44, 63–67.
- Marche, T., Snchitzer, M., Dinel, H., Pare, T., Champagne, P., Schulten, H.R., Facey, G., 2003. Chemical changes during composting of a paper mill sludge-hardwood sawdust mixture. *Geoderma* 116, 345–356.
- Natarajan, E., Nordin, A., Rao, A.N., 1998. Overview of combustion and gasification of rice husk in fluidized bed reactors. *Biomass and Bioenergy* 14, 533–546.
- Qafoku, N.P., Sumner, M.E., West, L.T., 2000. Mineralogy and chemistry of some variable charge subsoils. *Communications of Soil Science and Plant Analysis* 31, 1051–1070.

- Qafoku, N.P., Van Ranst, E., Noble, A., Baert, G., 2004. Variable charge soils: their mineralogy, chemistry and management. *Advances in Agronomy* 84, 159–215.
- Soil Survey Staff, 2010. *Keys to Soil Taxonomy*, 12th Edition. USDA, Washington, DC.
- Sposito, G., 1989. *The Chemistry of Soils*. Oxford University Press, New York.
- Von Uexkull, H.R., Mutert, E., 1995. Global extent, development and economic impact of acid soils. *Plant-soil interactions at low pH: principles and management*. In: Date, R.E., Grundon, N.J., Rayman, G.E., Probert, M.E. (Eds.), *Proceeding of third International Symposium on Plant-Soil Interactions at Low pH*, Brisbane, Queensland, Australia, pp. 5–19.
- Wershaw, R.L., Leenheer, J., Kennedy, K.R., Noyes, T.I., 1996. Use of ^{13}C NMR and FTIR for elucidation of degradation pathways during natural litter decomposition and composting: I. Early stage leaf degradation. *Soil Science* 161, 667–679.