Dissolution of Ground Basalt and Its Effect on Oxisol Chemical Properties and Cocoa Growth

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Abstract: Obtaining suitable and environmentally sound materials for restoring properties of highly weathered soils (e.g., Oxisols) presents a great challenge. A study was carried out to: (i) determine the ability of ground basalt to increase the negative charge of an Oxisol, increase plant nutrients (Ca, Mg, K, and Na), and suppress Al toxicity; and (ii) assess the effects of basalt application on cocoa growth. Pots containing 20 kg pot^{-1} of Oxisol were treated with various rates of finely ground basalt (<250 μm) and planted with cocoa (*Theobroma cacao* L.) in a greenhouse for 15 months. The soils and *in situ* soil solutions were sampled and analyzed periodically. The ground basalt continuously increased soil pH with increasing application rates. The cation exchange capacity occupied by base cations increased with increasing ΔpH value (soil pH $-$ pH$_0$), confirming that the type of charge generation depends mainly on variable charge. The cation exchange capacity occupied by base cations value for different basalt rates at any given similar equilibrium pH value always increased with increasing basalt rates, suggesting that every increment of basalt rates generated "new negative sites" to retain cations in the soil. Basalt application continuously released base cations, as revealed by the significant increases in Ca, Mg, K, and Na both in the forms of exchangeable cations and soluble cations (*in situ* solution), with concomitant suppression of toxic elements (Al and Mn). Basalt application significantly improved cocoa growth, suggesting that basalt is a promising material to be used for restoring the chemical properties of highly weathered tropical soils.

Key words: Oxisol, basalt, charge characteristics, nutrition, cocoa.

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The productivity of Oxisols, variable-charged soils, in Malaysia is low because of low cation exchange capacity (CEC), low basic cations, and high Al saturation (Anda et al., 2008a). Qafoku et al. (2004) reviewed variable-charge soils worldwide and suggested that their management should be focused on manipulation of surface charge characteristics to control retention of cations and anions. Attempt to obtain suitable and environmentally sound materials to be used for restoring the charge characteristics of highly weathered tropical soils is challenging. In Malaysia, dolomitic limestone is used to improve charge properties of Oxisols and Ultisols (Shamshuddin and Ismail, 1995), whereas bentonite clay has been used in Australia (Noble et al., 2001). Basalt, a naturally available basic rock, can be applied to the soils as an alternative. Interest in the efficacy of crushed basalt as a soil amendment has been ongoing. Gillman (1980) incubated variable-charge soils (Oxisols) with crushed basalt scoria and reported that after 12 months of incubation, there were increases in soil pH, CEC, and exchangeable cations (Ca, Mg, and K); these effects increased with incubation time. Further studies (Gillman et al., 2001; 2002) were performed using basalt dust in a 3-month laboratory experiment of seven highly weathered soils. The results showed increases in soil pH, CEC, and exchangeable Ca, Mg, and K, whereas active acidity and reserve acidity decreased.

Recently, Anda (2006) studied the effects of finely ground basalt on an Oxisol for 2 years under laboratory conditions. He reported that basalt significantly increased soil pH as well as generated new negative-charge sites. Another interesting finding was that basalt continuously released exchangeable cations as revealed by the increase in Ca, Mg, K, and Na (extracted by 1 *M* NH$_4$OAc). The corresponding cations in soluble forms were also increased, referred to as cation composition of *in situ* soil solution (solution obtained using rhizon soil moisture samplers). All these ameliorative effects of basalt application on soils were demonstrated with laboratory studies. Thus, there is justification to extend the experiment to greenhouse conditions to relate to crop growth.

In Mauritius, D'Hotman de Villiers (1961) reported that basalt-treated soils greatly increased sugarcane yield with concomitant long-term residue effects. Boniao et al. (2002) planted maize on two acidic Inceptisols (pH 5.3–5.8) treated with ground basalt pyroclastics and incubated for 9 months. They reported no significant change in soil CEC caused by basalt treatment. It was believed that a 9-month period was insufficient to observe the maximal effect of basalt application; a longer time was needed for basalt to disintegrate and release plant nutrients. The maximal effect occurs when all ground basalt is dissolved in the soil.

Increasing negative charge in the soils is an important issue for soil management. Soil charge characteristics, pH$_0$ and point zero net charge (PZNC), are useful in assessing the development of negative charge, positive charge, and all-charge generation on soil surfaces. The pH$_0$ is the pH at which the sum of charges caused by adsorption of potential-determining ions is zero. At this pH, there are equal amounts of negative and positive charges of the variable-charge component (Uehara and Gillman, 1980). The PZNC is the point of zero net charge for the whole soil. At this pH, there are equal amounts of negative and positive charges, irrespective of charge origin (Gillman, 2007). According to Gillman (2007), the coincidence of pH$_0$ and PZNC indicates zero net permanent charge, whereas pH$_0$ > PZNC and pH$_0$ < PZNC denote that the soil surfaces bear negative and positive net permanent charges, respectively.

Based on the available information, no systematic study has been carried out on highly weathered soils (under greenhouse conditions) to assess in detail the release of plant nutrients that affect crop growth from basalt into the soils. Likewise, the change in charge properties caused by basalt application has not been fully characterized. We hypothesize that basalt application

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on a highly weathered soil is able to generate new soil negative-charge sites and release various essential and beneficial elements for crop growth. The objectives of this study were to: (i) determine the ability of ground basalt to increase the negative charge of an Oxisol, increase plant nutrients (Ca, Mg, K, and Na), and suppress Al toxicity; and (ii) assess the effects of basalt application on the growth of cocoa.

MATERIALS AND METHODS

This experiment was carried out using Segamat soil (fine clayey, kaolinitic, isohyperthermic, Rhodic Hapludox), sampled from Jengka, Pahang, Malaysia. The topsoil (0–20 cm) was air dried, ground, passed through a 2-mm sieve, and used for pot experiment. The properties of Segamat soil used have been published elsewhere by Anda et al. (2008b). The soil contained 80% clay, 1.3% organic C, CEC (pH 7) of 7.6 $cmol_c$ kg^{-1}, and a pH of 4.2. Aluminium- and Fe-dithionite contents were 11.9 and 93.3 mg g^{-1}, respectively. Mineralogical compositions of the clay fraction were dominated by kaolinite, goethite, and hematite.

The basalt was supplied by Pacific Mineral Developments Pty Ltd, Australia, in the form of finely ground basalt rock. The particle sizes were ≤50 μm (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 ≤250 μm was used. Major chemical composition obtained from X-ray fluorescence analyses provided by the company were: CaO (8.97%), MgO (10.70%), K_2O (1.79%), Na_2O (2.59%), SiO_2 (43.20%), Al_2O_3 (12.90%), Fe_2O_3 (12.90%), P_2O_5 (0.77%), and SO_2 (<0.01%). According to Gillman et al. (2002), this particular basalt rock contains olivine (10%), plagioclase (12%), magnetite (10%), augite (30%), orthoclase (minor), apatite (0.5%), and altered glass (37%).

Basalt applications consisted of six rates (0, 5, 10, 20, 40, and 80 t ha^{-1}), which are referred to as B0, B1, B2, B3, B4, and B5, respectively. The soil was weighed (20 kg pot^{-1}), then thoroughly and homogeneously mixed with basalt according to a given treatment. Next, the soil was transferred into a pot, and soil moisture content was adjusted to 80% water-holding capacity. The experiment was arranged in a randomized complete block design with three replications. Cocoa (*Theobroma cacao* L.), KKM22 cultivar, was selected from the nursery after 1 month to obtain relatively uniform seedlings and 1 seedling/pot was grown as a test crop. The soil moisture was maintained at field capacity by daily watering. Soil subsamples and *in situ* soil solution were periodically taken for 15 months using a small stainless steel auger and a rhizon soil moisture sampler, respectively. For every sampling, about 80 g of soil (composite of four cores) was taken, air dried, ground, and kept for soil analyses. Agronomic observation included plant height, plant diameter, and dry matter weight (DMW) (roots, stems, and leaves). The fallen leaves were collected daily into a plastic bag attached to the pot and weighed when sufficient amount was obtained. The cocoa was harvested after 15 months.

In situ soil solution was sampled using a rhizon soil moisture sampler. This sampler consisted of a hydrophilic porous polymer and a connector for attaching a vacuum syringe (10 mL) to extract soil solution. An internal steel wire gave the sampler sufficient rigidity when inserted into the soil. The aliquot was used for electrical conductivity measurement using a conductivity meter and for pH measurement using a pH meter (Thermo Orion, Model 410 a). The Ca, Mg, K, Na, Si, Fe, Al, and Mn were determined using an inductively coupled plasma emission spectrometry.

The soil pH of natural soil after basalt treatment was measured in 1:10 soil–0.002 *M* $CaCl_2$ ratio. The generation of surface charge resulting from basalt treatment was determined by measuring pH_0 using potentiometric titration as described by Gillman (1984). Briefly, the soil was saturated with 0.1 *M* $CaCl_2$. The soil was then washed with 0.002 *M* $CaCl_2$ to reduce electrolyte concentration. The pH was adjusted to between 3.0 and 5.5 using HCl or $Ca(OH)_2$. When equilibrium occurred (4–5 days in this study), the pH was recorded as $pH_{0.002}$, and then 0.5 mL of 2 *M* $CaCl_2$ was added and shaken before pH was again recorded as $pH_{0.05}$. The position of pH_0 was obtained from the zero difference between $pH_{0.05}$ and $pH_{0.002}$ by interpolation.

Point zero net charge was determined from pH value where equal amounts of index cation and anion were adsorbed. The negative charge (CEC) and positive charge anion exchange capacity (AEC) was determined as described by Gillman (1984), except that the amounts of Ca^{2+}, Al^{3+}, and Ca^{2+} plus Al^{3+} adsorbed were referred to as basic CEC (CEC_B), acidic CEC (CEC_A), and total CEC (CEC_T), respectively (Gillman and Sumpter, 1986). The AEC was equal to amount of Cl^- adsorbed. The position of PZNC is the pH value where AEC value equals CEC_T. To determine the variation in negative and positive charges with pH, five portions of 2 g 2-mm air-dried samples were weighed into 50-mL preweighed centrifuge tubes, and the pH of the suspension was adjusted to between 2.5 and 5.0 as described for pH_0 measurement. However, after centrifugation of the third suspension, the supernatant solution was removed and retained for analyses of Ca, Al, and Cl. The tubes were weighed to estimate the volume of entrained solution. The soil was then extracted with 20 mL of 1 *M* NH_4NO_3, and Ca, Al, and Cl were determined in this supernatant solution. The Ca and Al were determined by atomic absorption spectrophotometer. The Cl was determined by titration with $AgNO_3$ as described by Van Ranst et al. (1999). The Ca, Al, and Cl were calculated, and then the amount of these ions in entrained solution was subtracted to account for amounts of Ca, Al, and Cl adsorbed. The pH value where Ca + Al adsorbed were equal to Cl adsorbed is the PZNC.

RESULTS AND DISCUSSION

Effect of Basalt on Soil pH and Variable-Charge Component

The effect of basalt application on the Oxisol was clearly shown by the significant increase in soil pH from 3.9 to 5.1, depending on basalt rate and duration of application (Fig. 1).
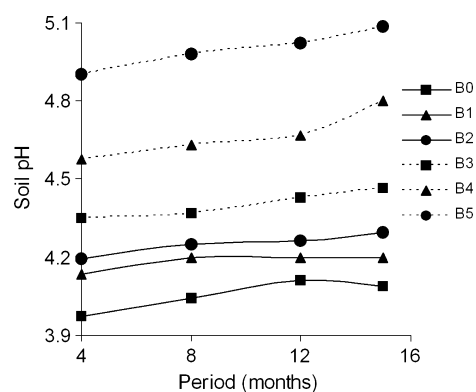

FIG. 1. The effect of basalt application on soil pH over a period of 15 months. Note that B0, B1, B2, B3, B4, and B5 are 0, 5, 10, 20, 40, and 80 t ha^{-1}, respectively.

The highest pH of 5.1 was achieved with 80 t ha^{-1} application after 15 months. Generally, the trend of each application rate indicated that the soil pH still consistently increased with increasing application time, suggesting the longer beneficial residual effect of basalt in increasing soil pH.

The effect of basalt treatments on the characteristics of variable-charge components (pH$_0$) of Oxisol grown with cocoa is given in Fig. 2. As expected, pH$_0$ values decreased with basalt application, but it decreased only 0.1 units at 40 and 80 t ha^{-1} for the first 8 months of growing period. For the following 12 and 15 months of the growing periods, the pH$_0$ values were relatively similar and decreased by 0.3 units each, depending on basalt application rates. This indicates that basalt application was able to generate variable negative charges on soil surfaces.

Effect of Basalt on Charge Generation of Whole Soil

The changes in PZNC, negative and positive charges at natural soil pH, after basalt application are given in Table 1. The PZNC decreased from 4.0 to 3.2 for Month 12 and from 3.8 to 2.7 for Month 15, depending on basalt application rate, indicating that basalt application generated negative charges. Generally, the magnitude of total negative charge (CEC$_T$) and net charge (N$_{et}$C) considerably increased with increasing basalt amendment rates (Table 1). For instance, at an application rate of 80 t ha^{-1}, the CEC$_T$ values increased from 3.6 to 5.0 cmol$_c$ kg^{-1} for Month 12 and from 3.5 to 5.2 cmol$_c$ kg^{-1} for Month 15. The corresponding values for the N$_{et}$C were 0.9 to 2.3 cmol$_c$ kg^{-1} and 1.1 to 3.2 cmol$_c$ kg^{-1}, respectively.

As expected, after basalt application (Months 12 and 15), the proportion of total negative charge (CEC$_T$) occupied by base cation (CEC$_B$) increased with increasing basalt rate, whereas the reverse is true for acid cation (CEC$_A$). Of the 5.0 cmol$_c$ kg^{-1} CEC$_T$ generated by basalt application at 80 t ha^{-1}, 4.8 cmol$_c$ kg^{-1} sites may be available to be occupied by base cations, leaving behind only 0.2 cmol$_c$ kg^{-1} sites to be occupied by reserved cation acidity (Al). This result would have major implications on agronomic practice with respect to exchangeable cations. In contrast to CEC$_T$ values that increased with basalt rates, the positive charge (referred to as AEC) decreased with increasing basalt rates, which were clearly shown at Month 15.

The mode of the increase in soil negative charges attributed to basalt application, whether it was caused by the increasing soil pH alone or basalt itself, was the provision of new negative-charge sites. The mode can be assessed by subjecting similar equilibrium pH values to different basalt rates and by determining the different magnitudes of charge generation. The charge generations at similar equilibrium pH values of different basalt rates are shown in Fig. 3. If the increase in CEC$_B$
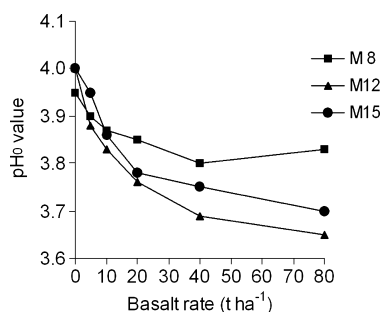
TABLE 1. Changes in PZNC, Total Charge, and Net Charge as Affected by Basalt Application at Natural Soil pH

| Treatment | PZNC | Soil Charge (cmol$_c$ kg^{-1}) | | | | |
		CEC$_B$	CEC$_A$	AEC	CEC$_T$	N$_{et}$C
Month 12						
B0	3.97	3.19	0.38	2.69	3.57	−0.88
B1	3.80	2.74	0.18	2.57	2.92	−0.35
B2	3.80	2.79	0.18	2.60	2.97	−0.37
B3	3.85	3.53	0.13	2.58	3.66	−1.08
B4	3.61	4.55	0.12	2.73	4.67	−1.94
B5	3.15	4.84	0.13	2.65	4.97	−2.32
Month 15						
B0	3.80	3.09	0.42	2.40	3.51	−1.11
B1	3.30	2.93	0.37	2.26	3.30	−1.04
B2	3.30	3.23	0.34	2.19	3.57	−1.38
B3	3.15	3.59	0.32	2.23	3.91	−1.68
B4	2.70	4.54	0.26	2.04	4.80	−2.76
B5	2.65	4.92	0.31	2.02	5.23	−3.21

AEC: positive charge; CEC$_A$: negative charge for acidic cation (Al adsorbed); CEC$_B$: negative charge for basic cation (Ca adsorbed); CEC$_T$: total negative charge (Ca + Al adsorbed); N$_{et}$C: net charge (AEC − CEC$_T$).

value was solely controlled by increasing soil pH values, then all data of basalt rates would fall on the single curve within the range of pH observed. However, this did not happen. Instead, at any given similar equilibrium pH value, the higher basalt rate always resulted in a higher CEC$_B$ value (Figs. 3A, B). For example, at an equilibrium pH 4.5 at Month 15, the soil CEC$_B$ values at B1 and B5 basalt rates were 2.9 and 4.0 cmol$_c$ kg^{-1}, respectively. The corresponding values at equilibrium pH 5.5 were 4.1 and 5.5 cmol$_c$ kg^{-1}. This finding clearly indicates that the increment of basalt rates would generate "new negative sites" to retain cations. Thus, the increase in negative charges attributed to basalt application occurred through the increased soil pH and generation of new negative sites.

In contrast to the negative charges (CEC$_B$) that increased with equilibrium pH, the positive charges (AEC) increased with decreasing equilibrium pH, but were only obvious at pH ≤4.0; at pH >4.0, the positive charge was relatively unchanged (Figs. 3C, D). The magnitude of AEC values after basalt treatment considerably decreased, depending on basalt rate, suggesting that basalt was able to reduce positive charges. For instance, a basalt application rate of 80 t ha^{-1} decreased the positive charge from 2.9 to 2.1 cmol$_c$ kg^{-1} at pH 3.0 and from 2.4 to 1.9 cmol$_c$ kg^{-1} at pH 5.0 after 15 months (Fig. 3D). At low-equilibrium pH zone (pH <4.0), the AEC value for B0 was higher compared with B1 and B2 treatments because of more protonation in the former, whereas for B1 and B2, less protonation caused by the blocking of positive-charge sites by silicate anion liberated from basalt.

The trends of decreasing positive charge with increasing pH values and basalt rates were very clear at 40 and 80 t ha^{-1} for Month 12 and all basalt rates for Month 15. However, the rates of 5 and 10 t ha^{-1} (B1 and B2) showed higher positive charges than the control at pH >3.5 for Month 12. These data may suggest the slow process of basalt reaction with the soil.

It is worthwhile to point out that at the end of the experiment (Month 15), for the control treatment (no basalt application), the magnitude of negative and positive charges was
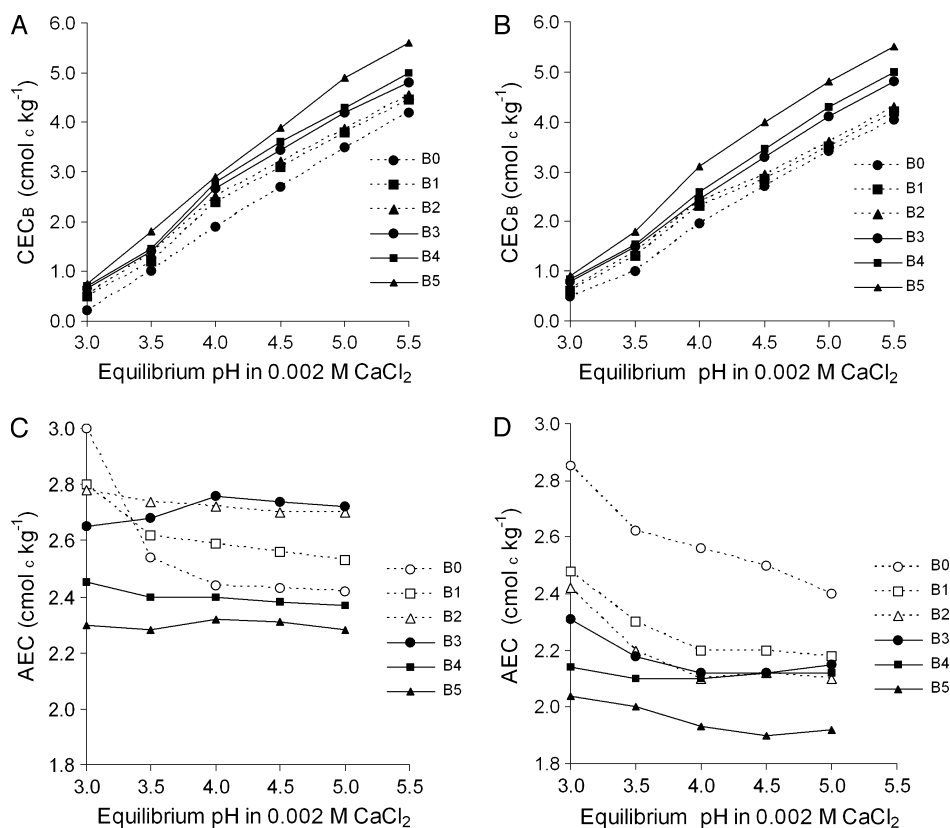
FIG. 2. The effect of basalt application on pH$_0$ after 8-, 12-, and 15-month growing periods. M: month.

FIG. 3. The CEC_B and AEC of adjusted equilibrium soil pH values (span from 3.0 to 5.5.) at different basalt rates during a period of 15 months: (A) CEC_B at Month 12, (B) CEC_B at Month 15, (C) AEC at Month 12, and (D) AEC at Month 15. Note that B0, B1, B2, B3, B4, and B5 are 0, 5, 10, 20, 40, and 80 t ha^{-1}, respectively.
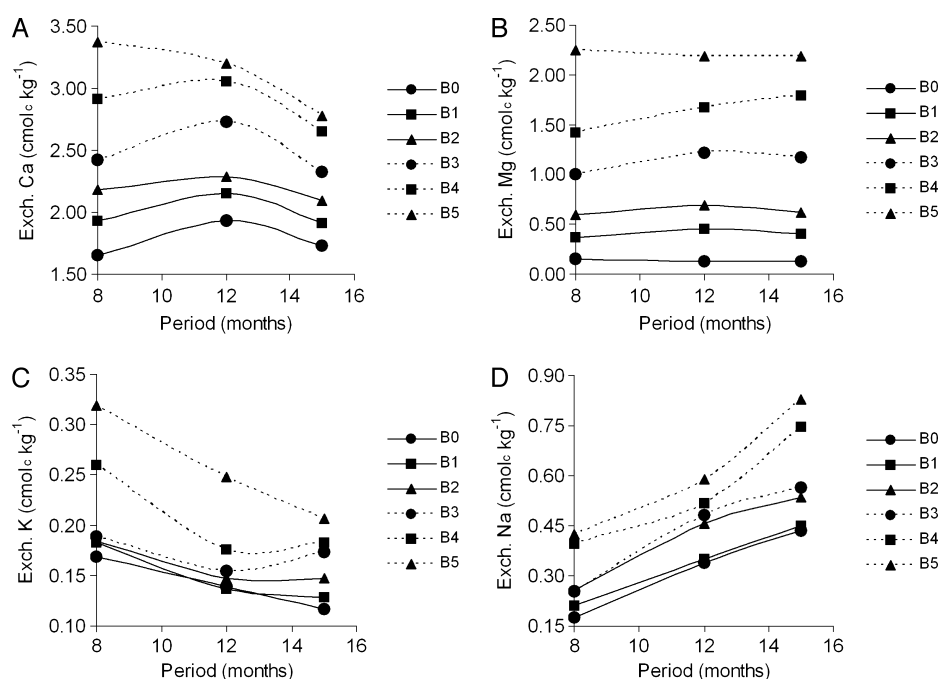

FIG. 4. The effect of basalt application on exchangeable cations at different application periods: (A) Ca, (B) Mg, (C) K, and (D) Na. Note that B0, B1, B2, B3, B4, and B5 are 0, 5, 10, 20, 40, and 80 t ha^{-1}, respectively.

TABLE 2. Summary Statistical Analysis of *In Situ* Soil Solution at Different Sampling Periods

Treatment	Ca	Mg	Na	K	Si	Al	Mn	pH	EC
Month 4									
Basalt	**	***	***	***	*	ns	nd	**	**
Month 8									
Basalt	**	***	***	***	nd	nd	***	*	**
Month 12									
Basalt	***	***	***	***	**	**	*	*	ns
Month 15									
Basalt	**	***	***	***	**	***	***	ns	**

ns, $P > 0.05$; *$P < 0.05$; **$P < 0.01$; ***$P < 0.0001$.
nd: not determined.

only slightly changed (i.e., the $N_{et}C$ was 1.1 cmol$_c$ kg^{-1}). Thus, one might expect that the Oxisol used in this study has very limited capability to retain cations.
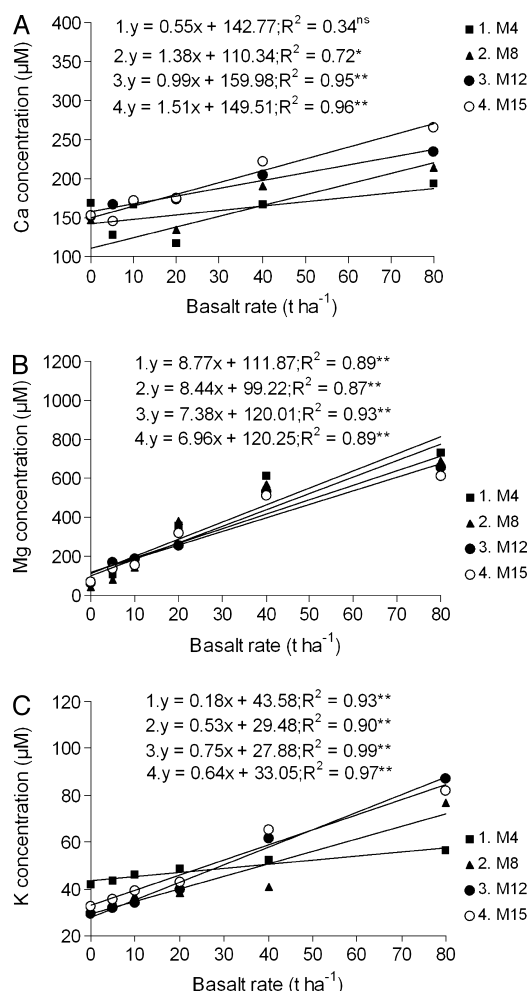
FIG. 5. The relationship between basalt application and ion concentration of *in situ* soil solution at different duration periods: (A) Ca, (B) Mg, and (C) K. M: month.
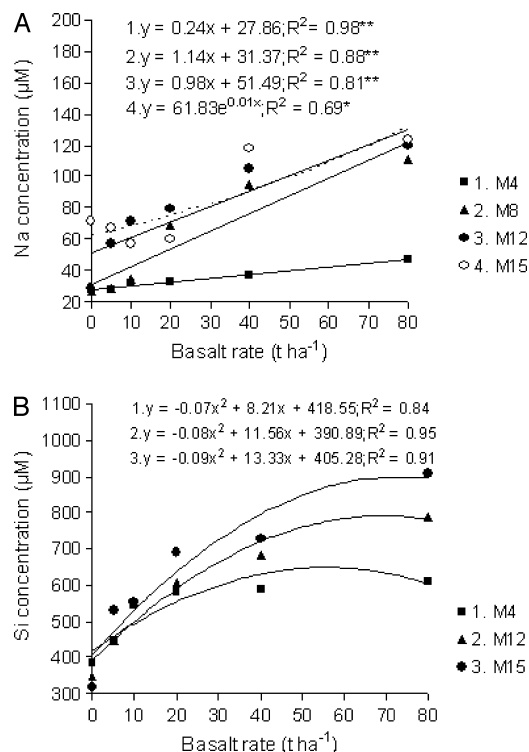
FIG. 6. Relationship between basalt treatments and ion concentration of *in situ* soil solution at different duration periods: (A) Na and (B) Si. M: month.

Release of Nutrients From Basalt

The release of various elements from dissolution of basalt was assessed by determining both exchangeable cations (extracted by 1 M NH$_4$OAc from solid phase) and soluble ions (measured from *in situ* soil solution sampling).

Release of Exchangeable Cations

Basalt application significantly increased the concentrations of exchangeable Ca, Mg, K, and Na ($P < 0.05$) (Fig. 4). Every basalt increment rate consistently increased the contents of exchangeable Ca, Mg, K, and Na. The magnitude of each cation released from basalt to the soil was assessed by subtracting the control treatment from each application of basalt rate in Fig. 4. Results indicated (data not shown) that at any period (from 8 to 15 months), the magnitude of the exchangeable cations released from finely ground basalt was in the order of Mg > Ca > Na > K. For example, at Month 15, the magnitude of Mg, Ca, Na, and K released were 0.27 to 2.06, 0.19 to 1.05, 0.01 to 0.39, and 0.01 to 0.09 cmol$_c$ kg^{-1}, respectively, depending on basalt rates. Logically, the magnitude of absolute exchangeable cations released from basalt should exceed the present measured concentrations because some portions had been absorbed by cocoa crops. Thus, the present exchangeable cations are more realistically called the remainder of basalt-released exchangeable cations.

The Release of Ions From Basalt Into Soil Solution

Basalt application significantly increased the concentrations of Ca, Mg, K, Na, and Si in the *in situ* soil solution, whereas the concentrations of Al and Mn were significantly decreased (Table 2). The effect of basalt rates showed positive linear relationships with Ca, Mg, K, and Na concentrations, with
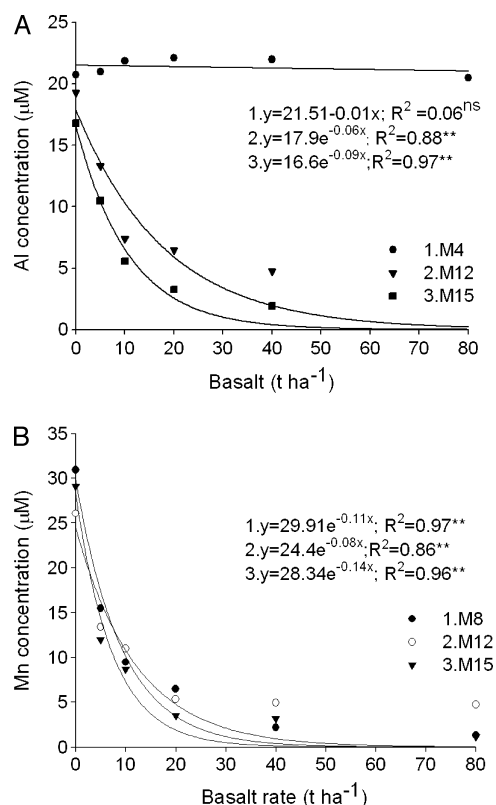
FIG. 7. Relationship between basalt treatments and ion concentration of *in situ* soil solution at different duration periods: (A) Al and (B) Mn. M: month.

insufficient solution), it is assumed that its trend would be the same to that of Mn. There was also evidence to show that basalt did not decrease Al in a short period as revealed by the data at Month 4 after basalt application (Fig. 7A), for which the Al concentration remained at about 21 μmol/L for all basalt application rates. This indicates that basalt dissolution in soils is slow as shown by Boniao et al. (2002). Thus, a longer period is needed to sufficiently suppress the Al in the soil solution to an acceptable level for a reasonable crop growth (as indicated by Month 12).

The Effect of Basalt Application on Cocoa Growth

Basalt application significantly increased the DMW of roots, stems, and leaves (Fig. 8). The significant increase was achieved at a basalt rate of 80 t ha^{-1} for roots and leaves, whereas the stem was at 10 t ha^{-1}. The fitting curves indicated positive quadratic relationships between basalt application and DMW of roots, stems, and leaves.

The determinant coefficients (R^2) of relationships between basalt rates with roots, leaves, and stems were 0.96, 0.85, and 0.85, respectively (Fig. 8). This indicates that the three cocoa compartments have different responses to basalt application. The response of roots showed that 96% of its improvement was accounted for by basalt, whereas for stem and leaves, they were 85% each. In other words, without basalt application, the root growth was reduced (highly sensitive to limiting factors of soil properties) compared with those of stems and leaves. This is probably caused by the presence of toxic elements, such as Al and Mn, in high concentrations in the absence of basalt application.

GENERAL DISCUSSION

The Effect of Basalt on Soil Charge Properties

Comparison of soil pH, pH_0, and PZNC after basalt application showed that the soil pH is higher than pH_0, indicating that soil surfaces bear negative variable charges. In all cases, the pH_0 values were higher than PZNC values, indicating that the soil surfaces also had negative permanent charge (Gillman, 2007). This implies that the capability of the highly weathered soil had an increased capacity to retain many base cations. This is meaningful if the acidic cation (e.g., Al) is

the exception of Na concentration at Month 15, which showed an exponential relationship (Figs. 5, 6). In addition, correlation between basalt rates and Si concentration had a quadratic relationship (Fig. 6B). This indicated that the Si began to probably form monomers or polymers of Si(OH)$_4$ when its concentration exceeded 650 μmol/L. Except for Ca (Month 4), generally, the determinant coefficients (R^2) of the fitting curves for all types of ions ranged from 0.81 to 0.99 (Figs. 5, 6), indicating that 81% to 99% of the variation of ion concentrations of the *in situ* soil solution was accounted for by basalt application. The R^2 values for Ca were lower (0.34) at Month 4, but R^2 values increased to 0.95 to 0.96 after the 12- and 15-month periods probably caused by the slow release of Ca from Ca-bearing minerals in basalt.

At the end of the experiment (Month 15), all ion concentrations increased and achieved their highest values (Figs. 5, 6). An attempt was made to compare the magnitude of individual ion released by subtracting the control treatment (B0 = 0 t ha^{-1}) from all basalt rates (B1–B5 = 5–80 t ha^{-1}) for any given ion. The results (data not shown) suggest that the proportion of basic cations was in the order of Mg > Ca > Na > K; and if the Si was included, the order of proportion would be Si > Mg > Ca > Na > K. Thus, it seems that Si is the dominant ion released from the basalt.

In contrast to Ca, Mg, K, Na, and Si that increased in concentration with basalt rates, the Al and Mn concentrations significantly decreased with increasing basalt application rates (Fig. 7). Both Al and Mn exponentially decreased with increasing basalt rates at Months 12 and 15. It is interesting to note that Mn started to decrease significantly at Month 8. Although Al was not determined at Month 8 (because of
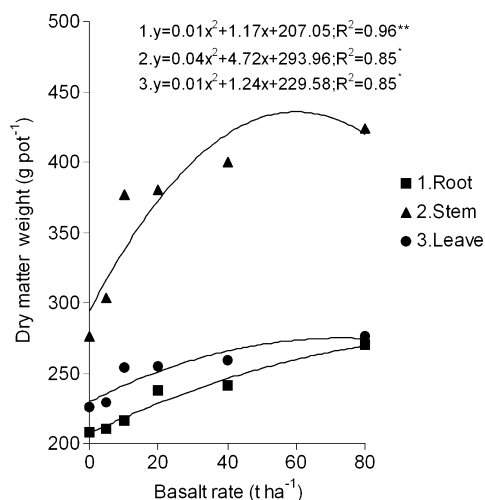

FIG. 8. Relationship between basalt rate and DMW of cocoa root, stem, and leaves.

suppressed by basalt application to avoid cation competition for the exchange sites.

The types of charge (variable or permanent) generated by basalt application could be assessed in two ways: (i) the variable-charge type if the charge generation depends on pH value, whereas the permanent charge is independent of pH value; and (ii) the difference in magnitude of positive charge and negative charge as measured by ion indices at pH_0. Figure 9 shows the increase in CEC_B value as the difference between soil pH and pH_0 values increased. This confirms the conclusion that surface charge is actually dependent on $pH-pH_0$, resulting in the development of variable-charge components.

By definition, the net variable charge resulting from the potential determining ions should be zero at pH_0; in other words, the magnitude of the negative charge is equal to the positive charge. Any difference in magnitude of negative and positive charges at pH_0 should be attributed to permanent charge. A comparison of the magnitude of negative and positive charges at pH_0 in Figs. 3A and B shows that the positive charge was greater than the negative charge for all basalt rates, with the exception of the 80 t ha^{-1} rate. This suggests the presence of positive permanent charge in the initial soil (control treatment) and that basalt application was able to compensate for this charge but only at high rates. Tessens and Zauyah (1982) found the existence of permanent positive charges in Malaysian Oxisols, attributed to Ti (IV) substitution for Fe (III) in goethite.

Basalt application on acid highly weathered soils produced a liming effect, that is, the soil pH increases, which in turn increases the negative charge. According to McBride (1994), the silicate anion (SiO_4^{-4}) liberated from minerals by hydrolysis is a very strong base, reacting with protons from solution to form weak acid, monosilicic acid (H_4SiO_4). These protons are provided by the ionization of water and produces OH^{-1}, resulting in the increase in the pH values.

The mechanism of the decrease in pH_0 and PZNC values attributed to basalt may be through adsorption of silicate anion on iron (hydro)oxides and Al surface functional group of clay mineral. The adsorption of silicate anion may block the positive-charge surfaces (Van Ranst, 1995). Jordan et al. (2007) has experimentally shown that the mechanism of silicate adsorption is by forming two types of surface complexes: first, the binding of neutral species (H_4SiO_4) on a neutral surface ($\equiv FeOH$) to form $\equiv FeH_3SiO_4$; and second, the deprotonation of silicate surface to form $\equiv FeH_3SiO_4^-$. In addition, according to Dietzel (1999), adsorption of silicic acid on surface hydroxyl could result in the formation of surface complexes according to the reaction: $\equiv AlOH^o + Si(OH)_4 = \equiv AlOSiO(OH)_2^- + H_2O + H^+$; where $\equiv AlOH^o$ denotes the surface hydroxyl group. This
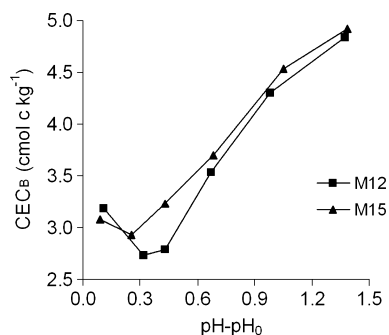
equation also indicates the generation of new negative-charge sites once adsorption of silicate anion occurs. This implies that more negative charge was created as adsorption of silicate anion increased, attributed to the increase in basalt rate application. The formation of surface complexes had probably resulted in the development of permanent charges.

Another interesting finding in this study is that the magnitude of total negative-charge generation was higher for Month 15 than Month 12 (Fig. 9), suggesting a long residual effect of basalt (at least 15 months, the end of experiment) in increasing soil negative charges.

The Release of Various Ions From Basalt

The application of basalt showed an increased concentration of Ca, Mg, K, and Na both in the forms of exchangeable cations and soluble cations (*in situ* solution) with increasing basalt application rates. In addition, the Si concentration increased, whereas Al and Mn of *in situ* soil solution decreased. This release of various essential and beneficial elements for crops may be associated with the mineral compositions of basalt. A previous study showed that the mineral composition of the basalt used in this study was plagioclase (12%), olivine (10%), augite (30%), orthoclase (minor), apatite (0.5%), and altered glass (37%) (Gillman et al., 2002). Based on the mineral composition of basalt, it is reasonable to conclude that the glass was an important source of nutrients in this study because it is easily weathered. In addition, it seems that Na was rapidly released from plagioclase (Na-Ca-feldspar) and augite ($[Ca,Na][Mg, Fe, Al][Si, Al]_2O_6$). Calcium may be derived from plagioclase and augite, whereas Mg was mostly from olivine ($[Mg, Fe]_2 SiO_4$) and augite. The low K of *in situ* soil solution was caused by the minor proportion of K-bearing mineral, that is, orthoclase ($KAlSi_3O_8$).

The relative rapid dissolution of minerals was affected by the nature of minerals (resistant or susceptible to weathering), particle size, and organic acids. Olivine, plagioclase, augite, and volcanic glass in basalt are minerals susceptible to weathering. Tropical conditions (high temperature in the greenhouse and moisture content was maintained at field capacity by daily watering) accelerate decomposition. The particle size of finely ground basalt was <50 μm (53%), 50 to 106 μm (26%), and 105 to 250 μm (14%). This small size allowed large surface areas for reaction and promoted rapid dissolution. The root density of cocoa was high in the pot. The roots released organic acids to dissolve minerals in basalt. Thus, it is believed that under tropical conditions, the small particle size of ground basalt and the presence of organic acids released by cocoa roots would have integral effects in speeding up basalt dissolution.

Generally, the improvement of the soil charge characteristics attributed by basalt application was revealed by decreases in pH_0 and PZNC values and increases in soil pH and ionic strength caused by cations released from basalt. Other factors were the blocking of positive sites by silicate anions and probably the fixation of phosphorus (0.77% P_2O_5 present in the basalt used).

Effect of Basalt Application on Cocoa Growth

Correlation analysis showed that basic cations (Ca, Mg, K, Na) and Si had positive linear relationships with DMW of cocoa, indicating that basalt application was able to increase plant nutrients in soil solution, which in turn, promoted cocoa growth (Fig. 8). In addition, a similar trend of relationship was shown by pH, where the DMW increased with the increase in soil solution pH values.

The concentration of toxic Al decreased because of an increase in soil pH caused by the hydrolysis of broken Si–O– bonds,

FIG. 9. The plot of CEC_B against ΔpH showing variable-charge type. Data points showed the increased basalt rate from left to right. M: month.

producing OH^-. The application of basalt lowered the Al and Mn ions to very low concentrations in soil (Fig. 8), which favors cocoa growth. In other words, basalt could alleviate the toxicity of Al and Mn for cocoa growth. All these findings indicated that low pH, low contents of various cations, and high concentrations of Al and Mn are limiting factors for cocoa growth in an Oxisol. All these limiting factors could be overcome by ground basalt application at a suitable rate.

CONCLUSIONS

Basalt improved soil charge characteristics by decreasing pH_0 and PZNC and by increasing soil pH, ionic strength, and blocking of positive sites by silicate anions. At any given similar equilibrium pH value but different basalt rates, the CEC_B always increased with increasing basalt rates, indicating that every increment of basalt rate would generate new negative sites to retain cations. The magnitude of total negative-charge generation was relatively similar for Months 12 and 15, that is, 3.5 to 5.2 $cmol_c$ kg^{-1}, depending on basalt rates. The magnitude of total negative-charge generation was still higher for Month 15 than for Month 12, suggesting a long residual effect of basalt application in increasing soil negative charges.

Under natural soil pH conditions, the Segamat soil had a considerable amount of positive charges, which decreased from 2.4 to 2.0 $cmol_c kg^{-1}$ under greenhouse conditions after 15 months following basalt application. However, the amount of negative charge of 3.5 $cmol_c kg^{-1}$ still slightly exceeded the positive charge without basalt application, resulting in a net negative charge of 1.1 $cmol_c kg^{-1}$.

Basalt application continuously released basic cations as revealed by the significant increases in Ca, Mg, K, and Na both in the forms of exchangeable cations and soluble cations (*in situ* solution), with concomitant decreases in toxic elements (Al and Mn). These phenomena resulted in significant improvements in the growth of cocoa, as shown by the increase in DMW of roots, stems, and leaves.

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