

Improving chemical properties of a highly weathered soil using finely ground basalt rocks



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ABSTRACT

Chemical property degradation of Oxisols (highly weathered soils) is revealed by very low cation exchange capacity and base cations but high Al saturation. The objective of this study was to increase cation exchange capacity and base cations and to alleviate Al toxicity of a highly weathered soil using finely ground basalt rocks. The topsoil and subsoil representing the natural and severely eroded conditions, respectively, were incubated with various rates (up to 80 t ha⁻¹) of finely ground basalt (<50 µm) under ambient laboratory conditions for 24 months. The soils and solution were sampled and analyzed periodically. Changes in soil surface charges were assessed by measuring point of zero charge (PZC) to account for variable charge generation and the point of zero net charge (PZNC) to account for all charge generations (variable and permanent charges). The soil solution was sampled using soil moisture samplers to observe cations released from basalt during each incubation period. Results showed that incubation of an Oxisol with finely ground basalt decreased PZC from 3.9 to 3.5 for the topsoil and from 3.9 to 3.7 for the subsoil. Corresponding values for PZNC measurements decreased from 3.05 to 2.52 for the topsoil and from 3.60 to 2.55 for subsoil. The decrease in PZC and PZNC values showed that basalt application was able to increase soil surface negative charge, while in turn increasing soil cation exchange capacity. At a given similar equilibrium pH value, increasing basalt rates showed an increased net negative charge (N_{et}C) from 0.0–6.3 to 3.2–8.7 cmol_c kg⁻¹, depending on basalt rates. This indicates that each increment of basalt rates generated “new negative sites” on soil surfaces to retain cations. At natural soil pH representing field conditions, the N_{et}C sharply increased from 1.5 to 10.1 cmol_c kg⁻¹ after basalt application. The higher N_{et}C values for the natural condition than the given equilibrium pH values were owing to the higher soil pH values in the former. Interestingly, the total negative charge (CEC_T) values were comparable to the negative charge occupied by base cations (CEC_B) at basalt incubation rates of ≥ 10 t ha⁻¹, indicating that base cations released from basalt successfully displaced acidic cations (e.g. toxic Al) on the soil exchange complexes. Cations released from basalt were revealed by the significant increases in Ca, Mg, K and Na both in the forms of exchangeable cations (measured from the solid phase) and soluble cations (measured from the soil solution), with concomitant reduction in Al and Mn contents. Hence, finely ground basalt is a promising natural material that can be used to restore negative charge and base cations and suppress Al and Mn contents of highly weathered soils, which in turn, have a great impact on preventing cation leaching, increasing soil nutrient availability and reducing elemental toxicities.

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1. Introduction

Oxisols are severely chemically degraded soils. According to von Uexkull and Mutert (1995) their distribution occupied 727 million ha (18.4%) of the total world's acid soils (3950 million ha). Agricultural practices, especially in tropical regions, mostly rely on Oxisols with very low productivity without technology intervention. A great

challenge in using Oxisols for agricultural activities is to obtain natural materials with a special ability to restore productivity.

Basalt rocks contain various essential elements (Ca, Mg, K, P, S and Fe) and beneficial elements (Na and Si) for crops. Basalt rocks are naturally available (Gillman, 1980; Gillman et al., 2002; Klein, 2002) and are environmentally sound as a soil amendment. Interest in the efficacy of crushed basalt to amend poor soils (especially highly weathered soils) and improve crop growth has been shown by D'Hotman (1961) who reported that basalt-treated soils remarkably increased sugarcane yield in Mauritius with concomitant long residue effect. A subsequent study was carried out by Gillman (1980) in Australia using variable charge soils (Oxisols) treated with crushed basalt scoria and reported that there

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were increases in soil pH, cation exchange capacity (CEC), exchangeable cations (Ca, Mg and K) after 12 months of incubation and these effects increased with incubation time. Later, Gillman et al. (2001, 2002) studied the effect of basalt dust incubation during three months of laboratory experiments on cation chemistry of seven highly weathered soils and reported the increase in soil pH, CEC and exchangeable Ca, Mg and K while active acidity and reserve acidity decreased.

Boniao et al. (2002) incubated two acid Inceptisols (pH 5.3–5.8) with ground basalt pyroclastics and calcium silicate for 9 months and reported that no significant change in soil CEC due to basalt treatment, whereas calcium silicate significantly increased soil CEC. In addition, the pH_0 values were significantly increased and the magnitude was much higher for calcium silicate treatment than for ground basalt. They stated that 9 months were insufficient time to observe maximal effect of treatments. From the literature, the effect of basalt on soil properties has been studied for 3–12 months with different degrees of effects. The inconsistencies in the above previous studies could have arisen because of insufficient incubation times to demonstrate the full effects, the fineness of the basalt powder or the particular type of basalt. Hence, the current study was conducted using finely ground basalt (<50 μm) and over a longer period of time, 24 months.

Negative surface charge of soils consists of permanent negative and variable negative charges (Skylberg and Borggaard, 1998) playing a major role in retaining the positively charged cations. The types of charge present in soils are controlled by type of mineralogical composition. The dominant minerals of highly weathered soils such as Oxisols are kaolinite with some gibbsite, goethite and hematite (Anda et al., 2008; Charlet and Sposito, 1987; Fontes et al., 1992; Herbillon, 1980; Melo et al., 2001). These minerals possess amphoteric surfaces and their surface charge could be positive, negative or zero depending on activities of potential-determining ions (H^+ and OH^-) and electrolyte concentrations of the surrounding solution (Chorover and Sposito, 1995; van Olphen, 1977). The pH value where there are equal amounts of negative and positive charge of variable charge components is referred to as pH_0 , while the pH value where equals amounts of negative and positive charge for all charge components (variable and permanent charge) is referred to as the point of zero net charge (PZNC) (Uehara and Gillman, 1981). According to Gillman (2007) permanent charge (negative or positive) is the structural charge related to isomorphous substitution during crystal formation. Varying the pH or ionic strength of the surrounding solution does not alter this charge. In addition, variable charge (negative or positive) is the charge that develops mainly on surface hydroxyl groups by protonation and deprotonation reactions. In highly weathered soils, the variable charge is dominant over the permanent charge on colloidal surfaces (Uehara and Gillman, 1981).

Total soil surface charges are usually measured using a non-specific ion adsorption so called indifferent electrolyte to observe changes in the electrostatic adsorption of a cation and anion index with changes in the activities of H^+ and OH^- , to find the point of zero net charge (PZNC) (Marcano-Martinez and McBrid, 1989; Parker et al., 1979; van Raij and Peech, 1972). For the soil variable charge, it is measured from potentiometric titration, that is, the point (pH_0) where soil pH values are similar in different electrolyte concentrations (Gillman, 2007). According to Appel et al. (2003) pH_0 or point of zero salt effect (PZSE) and PZNC are reliable parameters for measuring soil surface charges as have been proven from analyses of Oxisol, Ultisol, mineral standard kaolinite and synthetic goethite. They used potentiometric titration and reported pH_0 values were 2.8 for kaolinite and 7.9 for goethite. The corresponding values for PZNC were 2.7 for kaolinite and 7.4 for goethite, which are comparable to those reported in literature.

Highly weathered tropical soils consisted of a complex mixture of amphoteric solid inorganic and organic surfaces (Chorover and Sposito, 1995). Amphoteric properties refer to surface charge that can bear either positive charge in an acid condition or negative charge in an alkaline condition (Qafoku et al., 2004). In variable charge soils, the net surface charge (N_{etC}) is negative, zero or positive if soil pH is higher

than pH_0 , equal pH_0 , or lower than pH_0 , respectively (Uehara and Gillman, 1981). The pH_0 and PZNC parameters can be used to determine the presence of permanent charge on soil surfaces. If pH_0 value is equal, higher or lower than PZNC value denotes soil surfaces bear zero, negative, or positive permanent charge, respectively (Gillman, 2007). This has been tested using synthetic goethite, where the pH_0 equals PZNC indicating zero permanent charge of goethite surfaces.

It appears that Oxisols strongly need technology and amendment to manipulate their negative surface charge properties. However, to date no systematic long-term experiment that has been carried out to follow the ability of basalt and its residual effect to restore chemical properties of Oxisols. The objective of this study was to increase cation exchange capacity and base cations and to alleviate Al toxicity of a highly weathered soil using finely ground basalt rocks. We used an innovative technique, i.e., the soil solution was sampled using a rhizon soil moisture sampler in addition to a classical exchangeable cation measurement to follow the release of cations from basalt. It was expected that the long-term laboratory experiment of 24 months would allow the basalt to perform its potential full effect in manipulating the surface chemistry of Oxisol colloids.

2. Materials and methods

The experiment was carried out using a fine clayey, kaolinitic, isohyperthermic, Rhodic Hapludox (Segamat Series), which was sampled from Jengka, Pahang, Malaysia. The relevant properties of the studied Oxisol were assessed by digging a soil profile and collecting samples from each horizon for chemical and mineralogical analyses. The samples were air-dried, ground, passed through a 2 mm sieve and used for chemical and mineralogical analyses.

For laboratory experiments, the bulk samples of the topsoil (0–20 cm) and subsoil (20–40 cm) were taken to represent soils under normal condition (existing field conditions) and severely experienced erosion, respectively. The bulk soil samples were air-dried, ground, passed through a 2 mm sieve and used for incubation experiments.

Finely ground basalt used in this study was supplied by the Pacific Mineral Developments Pty. Ltd., Australia. The particle sizes were < 50 μm (53%), 50–106 μm (26%), 105–250 μm (14%), 250–500 μm (5%) and 500–2000 μm (2%). We used the small particle sizes of $\leq 50 \mu\text{m}$ in this study to allow rapid reaction of basalt with chemically degraded Oxisols. According to Gillman et al. (2002), this particular primary rock contained olivine (10%), plagioclase (12%), magnetite (10%), augite (30%), orthoclase (minor), apatite (0.5%) and altered glass (37%). The major chemical compositions obtained from X-ray fluorescence (XRF) 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%).

A factorial experiment of 2 x 6 with three replications was arranged in a completely randomized design (CRD). The experiment consisted of two soil layers (topsoil and subsoil) and six rates of basalt (0, 5, 10, 20, 40 and 80 t ha^{-1} , designated as B0, B1, B2, B3, B4 and B5, respectively). One kg of the ground soil ($\leq 2 \text{ mm}$ size) was weighed into each pot. Basalt rates were 0, 2.5, 5, 10, 20 and 40 g per pot, corresponding to the B0, B1, B2, B3, B4 and B5 rates, respectively. The soil and basalt were thoroughly and homogeneously mixed using a plastic tray prior to be transferred into a pot. Soil moisture content was adjusted to 80% water holding capacity using de-ionized water. The pot was covered to prevent evaporation and was incubated for 24 months in a dark room to prevent mold growth. Sub-samples were taken every three months for a period of 24 months, using a small stainless steel auger (1.5 cm internal diameter with 40 cm length). For each sampling, approximately 80 g soil (composite of four cores) was taken, air-dried, ground and kept for soil analyses. For further presentation all basalt rates were expressed in t ha^{-1} and not in g pot^{-1} .

The release of various ions from basalt dissolution into soil solution was determined every three months by sampling the soil solution,

coinciding with the time of soil sampling. The soil solution was sampled first and then followed by soil sampling as described previously. The soil solution was sampled using a rhizon soil moisture sampler (Rhizosphere Research Products, Wageningen, The Netherlands). 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 to be inserted into the soil. After extraction of a 10 ml soil solution aliquot from a pot at each solution sampling period, 10 ml of distilled water was evenly added to soil surface in the pot to compensate the extracted soil solution and maintain field capacity moisture content. The aliquot was used for electrical conductivity measurement using a conductivity meter and pH measurement using a pH meter (Thermo Orion, Model 410a). The Ca, Mg, K, Na, Si, Al, and Mn in the solution were determined using an inductively-coupled plasma optical emission spectrometry (ICP-OES).

The particle size of the soil was determined by a pipette method after removal of organic matter and iron oxides as described by [Sheldrick and Wang \(1993\)](#), organic C by combustion technique ([Merry and Spouncer, 1988](#)), N by Kjeldhal method ([Bremner and Mulvaney, 1982](#)). Aluminium was extracted with 1 M KCl ([Barnhisel and Bertsch, 1982](#)) and exchangeable cations by 1 M NH_4OAc buffered at pH 7 ([Soil Survey Staff, 1992](#)). The contents of Al, Ca, Mg, K and Na in the solutions were measured by atomic absorption spectrophotometer (AAS). The Al saturation was calculated as exchangeable Al divided by effective CEC. After exchangeable cations were extracted, the CEC was determined by displacing the NH_4^+ ions using 0.05 M K_2SO_4 and the measured NH_4^+ was considered as a measure of CEC. All measurements were carried out in duplicates.

Clay fraction for X-ray diffraction (XRD) analysis was prepared by dispersion with 2% Na_2CO_3 and no pretreatment with H_2O_2 and CBD were employed in order to allow determination of both phyllosilicates and sesquioxides minerals ([Jones and Malik, 1994](#)). Mg-saturated clays were prepared as oriented specimens and mounted on glass slides and run on Philips PW 3040/60 X'pert Pro X-ray diffractometer, using CuK -alpha radiation target, operated at 40 kV and 30 mA. The oriented specimens were scanned from 3 to $45^\circ 2\theta$ at $1^\circ/\text{min}$. XRD data were collected and stored by IBM compatible PC. Semi-quantitative estimation of the mineral proportion was calculated from the height of a first peak order times the width at half height ([Karanthanas and Hajek, 1982](#)).

For the soil charge generation attributed by basalt incubation, two charge parameters, i.e., point of zero charge of variable charge component (PZC or pH_0) and point of zero net charge (PZNC) of all charges (variable and permanent charges) were measured. The pH_0 was measured using potentiometric titration as described by [Gillman \(1984\)](#). Briefly, 2 g soil (2-mm air-dried sample) was added to each of five pre-weighed polyethylene centrifuge tubes and then saturated with 20 ml of 0.1 M CaCl_2 . The soil was then washed three times with 20 ml of 0.002 M CaCl_2 to reduce the electrolyte concentration to ionic strength of 0.006, which was considered representing field conditions. Next, the soil pH was adjusted to between 3.5 and 6.5 using HCl or $\text{Ca}(\text{OH})_2$. When equilibrium occurred (4–5 days in this study), the pH was recorded as $\text{pH}_{0.002}$ and then 0.5 mL of 2 M CaCl_2 was added and shaken before pH was again recorded as $\text{pH}_{0.05}$. The position of pH_0 was obtained from the zero difference between $\text{pH}_{0.05}$ and $\text{pH}_{0.002}$ by interpolation. For soil pH of natural soil treated with basalt, it was measured in 1:10 soil:0.002 M CaCl_2 ratio.

The 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 cation exchange capacity, CEC) and positive charge (referred to as anion exchange capacity, AEC) were 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 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.

The soil PZNC value of each basalt incubation rate was measured by spanning pH over the range of 2.5–5.0 and referred to as charge measurement at equilibrium conditions. The procedure was similar to pH_0 measurement, except that after last washing with 0.002 M CaCl_2 the pH of the suspension was adjusted between 2.5 and 5.0 as described for pH_0 measurement. Once the equilibrium pH was achieved, the supernatant solution was removed by centrifugation 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 in the supernatant solution were determined. The Ca and Al were measured using AAS, while Cl was determined by colorimetric titration with AgNO_3 as described by [Van Ranst et al. \(1999\)](#). These Ca, Al and Cl were calculated and then subtracted by the amount of these ions in entrained solution to account for the amounts of Ca, Al and Cl adsorbed. The pH value where Ca + Al adsorbed were equal to Cl adsorbed on soil surfaces is the point of zero net charge (PZNC). The amounts of Ca and Ca + Al adsorbed on exchange sites are referred to as negative charge occupied by base cations (or base cation exchange capacity, CEC_b) and total negative charge (CEC_T), respectively. The amount of Cl adsorbed is referred to as total positive charge (AEC). The net charge (NetC) was calculated as the difference between AEC and CEC_T ([Gillman and Sumpter, 1986](#)).

In addition, the magnitude of CEC_b , CEC_T , AEC and NetC was measured under natural soil pH condition (i.e., without equilibration over pH ranges) to observe variation of soil surface charge owing to variations of basalt rates that could represent the real situation in the field. Those parameters were measured in a similar manner to PZNC measurement with the exception that the soil pH was not spanned over the range of 2.5–5.0.

In anticipating the formation of amorphous material attributed by basalt treatments, the amorphous material was measured using ammonium oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, as described by [Van Ranst et al. \(1999\)](#). Briefly, 0.5 g soil was shaken with 50 ml extraction solution (a mixture of 0.2 M ammonium oxalate and oxalic acid solution, pH 3.0) for 2 h in the dark room. The mixture was centrifuged at 4000 rpm for 10 minutes and the contents of Fe, Al and Si in the supernatant solution were measured by ICP-OES.

Cations released from basalt were measured both in exchangeable and soluble forms. The former was measured by leaching the basalt treated-soils with 1 M NH_4OAc followed the method similar to a routine exchangeable cation measurement ([Soil Survey Staff, 1992](#)). Exchangeable cations were measured in supernatant solution using AAS. Soluble cation forms were measured from soil solution which was sampled using a rhizon soil moisture sampler as described previously.

All data were analyzed using SAS software version 8 (1999), Institute Inc., Cary, N. C, USA. The difference between mean values of basalt rates and of incubation periods for a given soil property was determined using Duncan multiple range test (DMRT). The correlation between soil properties against basalt rates and incubation periods was plotted using Microsoft Office Excel 2007.

3. Results and discussion

3.1. Soil pH and exchangeable Al

Relevant properties of an Oxisol profile used in this study showed high clay content (79–84%), very low CEC ($< 3.2 \text{ cmol}_c \text{ kg}^{-1}$) and cation content (sum of cations $< 0.40 \text{ cmol}_c \text{ kg}^{-1}$) at natural conditions but high Al saturation (77–83%) within the upper two soil horizons (0–45 cm) ([Table 1](#)). Mineralogical composition of the soil clay fraction showed the predominance of kaolinite (75–84%) accompanied by minor amounts of goethite and hematite. All these chemical properties and mineralogical compositions revealed that the soil has experienced intense, long-term weathering and leaching, which resulted in low soil productivity.

Basalt incubation for a period of 24 months remarkably increased soil pH from 3.9 to 6.5 for the topsoil and from 3.9 to 6.6 for the subsoil,

Table 1

Relevant chemical properties and mineralogical composition of Segamat soil used in this study.

Horizon	Depth (cm)	Particle size			C	N	pH ^a H ₂ O	Al	Exchangeable cation				CEC ^b		ECEC ^c	Al.sat	Mineralogy ^d			
		Clay	Silt	Sand					Ca	Mg	K	Na	pH 7	pH _n			Ka	Gb	Gt	Ha
		%							cmol _c kg ⁻¹								%			
A	0–14	79	17	3	1.4	0.13	4.19	1.41	0.15	0.23	0.02	nd	7.6	2.7	1.82	77.4	83	nd	11	6
Bo1	14–45	81	15	3	1.0	0.10	4.27	1.12	0.09	0.11	0.02	nd	7.6	3.2	1.35	82.9	84	nd	10	6
Bo2	45–85	82	15	3	0.9	0.08	4.25	0.38	0.09	0.14	0.02	nd	7.5	3.9	0.63	61.1	77	nd	15	8
Bo3	85–117	81	16	3	0.8	0.07	4.49	0.16	0.08	0.19	0.02	nd	7.2	2.4	0.45	34.9	75	nd	16	9
Bo4	117–165	84	13	3	0.8	0.05	4.58	0.16	0.10	0.08	0.02	nd	7.3	3.5	0.36	44.2	81	nd	13	6

nd = not detected;

^a pH measured in H₂O (1:2.5).^b Cation exchange capacity (CEC) pH 7 measured in NH₄OAc pH7; pH_n measured in 1 M NH₄Cl at natural soil pH (unbuffered).^c ECEC = Effective cation exchange capacity is sum of Ca, Mg, K, Na and Al.^d Ka = kaolinite, Gb = Gibbsite; Gt = Goethite; Ha = Hematite.

increasing values with basalt rates and the length of incubation time (Fig. 1). However, there was no significant effect of interaction between basalt rates and soil layers, suggesting that basalt increased pH of topsoil and subsoil in a similar way. In all cases, soil pH values significantly increased with basalt rates at any incubation period. With increasing incubation periods, the magnitude of soil pH values showed trends relatively constant for basalt rates of < 20 t ha⁻¹, indicating that the residual effect of these rates in maintaining soil pH could take place over 24 months or longer. Further increase in incubation rates to 40 and

80 t ha⁻¹, pH values still continuously increased with time until the end of the experiment. For example, the pH values of topsoil treated with basalt at 80 t ha⁻¹ (B5) increased from 3.9 to 5.5 by month 3 and continuously increased to 6.5 by month 24. The increase in soil pH was attributed to the release of silicate from basalt which was subsequently hydrolyzed. According to McBride (1994), the silicate anion (SiO₄⁴⁻) liberated from minerals is a very strong base, reacting with protons from solution to form weak acid, monosilicic acid (H₄SiO₄). The protons are provided by dissolution of water and produces OH⁻ ions, resulting in the increase of pH values.

Basalt incubation significantly decreased exchangeable Al for topsoil and subsoil after 12 and 24 months of incubation (Fig. 2). Exchangeable Al decreased from 0.60 to 0.35 cmol_c kg⁻¹ at the basalt rate of 5 t ha⁻¹.

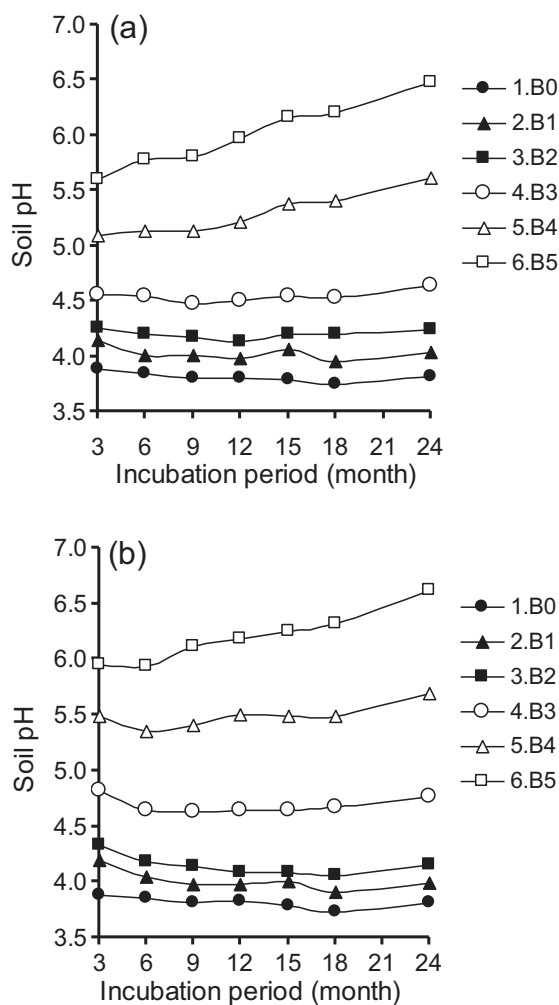


Fig. 1. The effect of basal application on soil pH over an incubation period of 24 months: (a) topsoil and (b) subsoil. Note: B0, B1, B2, B3, B4 and B5 are 0, 5, 10, 20, 40 and 80 t ha⁻¹, respectively.

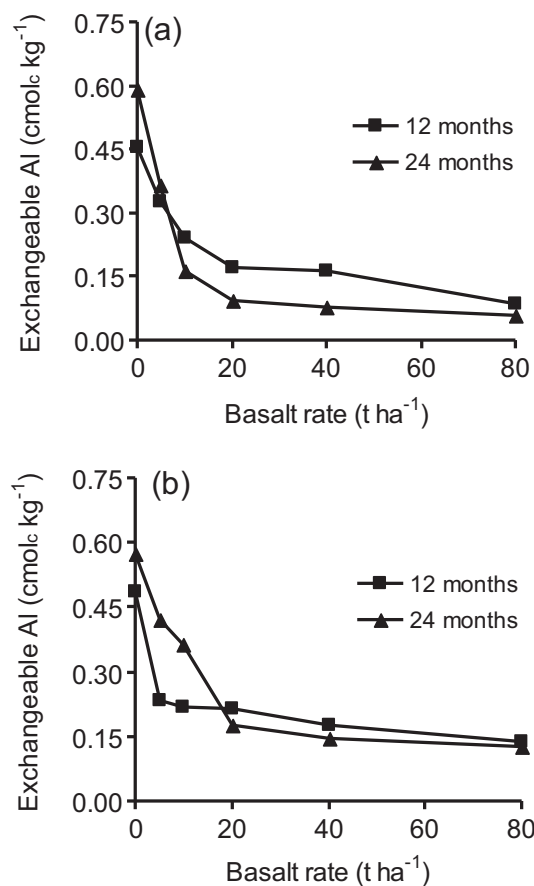


Fig. 2. Effect of basalt application on exchangeable Al (reserved acidity) over an incubation period of 24 months: (a) topsoil, (b) subsoil. Note: Rates of 0, 5, 10, 20, 40 and 80 t ha⁻¹, correspond to B0, B1, B2, B3, B4 and B5 symbols, respectively.

As basalt rate was raised to 10 t ha^{-1} , exchangeable Al continuously decreased and achieved relatively constant values at $20\text{--}80 \text{ t ha}^{-1}$ rates. It seems that basalt rate at 10 t ha^{-1} was sufficient to bring exchangeable Al to a low value (approximately $0.20 \text{ cmol}_c \text{ kg}^{-1}$).

3.2. Charge generation on variable charge component

Variable charge characteristic, (interchangeably referred to PZC or pH_0), is the pH value where the net total charge of variable charge component is zero, i.e. equal amount of potential determining ions (H^+ and OH^-) adsorbed on amphoteric surfaces and clay mineral edges. The effect of basalt incubation on Oxisols showed no considerable changes in pH_0 values of topsoil for the periods of 6 and 12 months compared to the control treatment (Fig. 3a). However, after 12 months, the basalt rates at $10\text{--}80 \text{ t ha}^{-1}$ (B2 to B5) were able to lower pH_0 . At the end of incubation (24 months) the pH_0 has decreased from 3.9 to 3.5 with the lowest pH_0 value occurred at basalt rates of 20 and 40 t ha^{-1} . The highest basalt rate of 80 t ha^{-1} showed slightly higher pH_0 value (3.6) than 20 and 40 t ha^{-1} rates. This indicates that basalt was able to generate soil negative charge of variable charge component although the reaction was rather slow.

In contrast to the topsoil, the effect of basalt incubation for the subsoil (representing severely eroded situation) increased pH_0 from 4.2 to 4.7 for month 12 and from 4.2 to 5.1 for month 18 (Fig. 3b) and that trend increased with increasing basalt rates. However, pH_0 values sharply decreased (mostly one unit decreased for each application rate) from months 18 to 24. It seems that there was a transition reaction product of basalt occurring for the subsoil (which was not occurred in the topsoil), to account for the increase in pH_0 during the first

18 months. This difference could be related to the formation of amorphous material having a high pH_0 value, which was verified by extracting amorphous materials after 18 months of incubation. The results showed that the concentrations of amorphous Si, Al and Fe increased with increasing basalt incubation rates (Fig. 4). This indicates amorphous materials were being formed, which in turn, resulted in an increase in 'oxide' sites, i.e. an increase in variable charge surfaces.

The increase in negative surface charge could be explained by adsorption of silicate released during basalt dissolution onto Fe and Al oxides to produce surfaces containing greater concentrations of hydroxyl groups that have a lower point of zero charge than those associated with the original oxides. Thus, as the point of zero charge (pH_0) decreases, the surface negative charge at any fixed point will increase. Our results did indeed show that pH_0 decreased when basalt incubation rate exceeded 10 t ha^{-1} . At the end of experiment, pH_0 decreased from 3.9 to 3.5.

The decrease in pH_0 values for the topsoil was related to amount of organic matter which is higher than the subsoil. This organic matter competes with Si to form complexes with Al. In the subsoil, Si released from basalt could form complexes with Al, due to the less competition between Si and organic matter for Al. Parfitt et al. (1999) used ^{13}C -NMR to study the interactions of soil organic matter with Al and allophane in Podzols and suggested that the carboxyl groups in the organic matter are bonded to structural Al on the surface of allophane spherules. If this is true, then the higher organic matter in the topsoil of the present study was successful to compete with Si to form a complex with Al, reducing the formation of Si-Al amorphous materials.

3.3. Charge generation on whole soil surfaces

The point of zero net charge (PZNC) is used to assess charge generation on the whole soil surfaces (deriving from variable and permanent charges). The PZNC values decreased with increasing basalt rate and incubation periods (Table 2). For month 12, PZNC decreased from 3.1 to 2.5 for the topsoil and from 3.6 to 2.6 for the subsoil. The corresponding values for month 24 decreased from 2.8 to 2.5 for the topsoil and from 2.9 to 2.5 for the subsoil. The PZNC values further decreased with increasing incubation time to month 24 for incubation rates of $\leq 20 \text{ t ha}^{-1}$ while PZNC values at 40 and 80 t ha^{-1} rates were already relatively constant (at a value 2.5). These evidences indicated that basalt

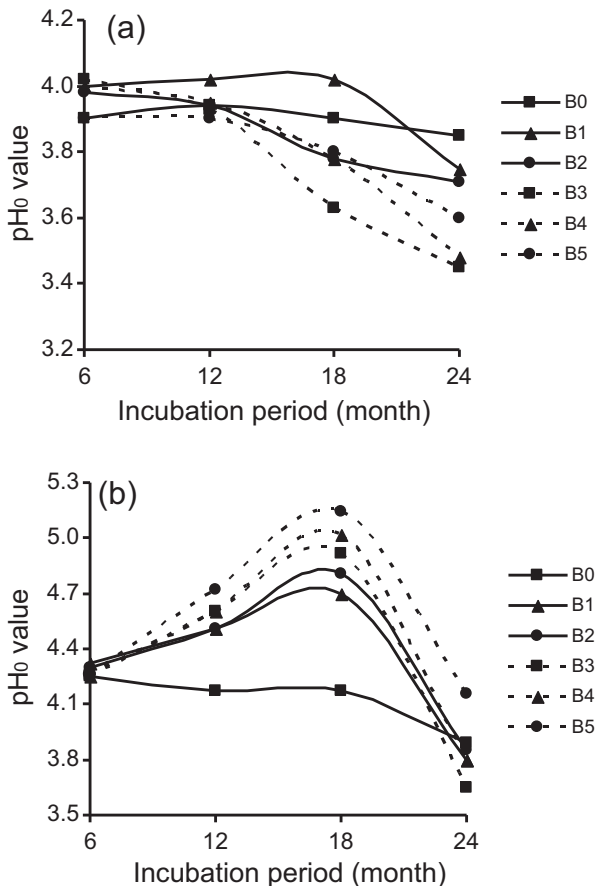


Fig. 3. Effect of basalt application on pH_0 over an incubation period of 24 months: (a) topsoil, (b) subsoil. Note: B0, B1, B2, B3, B4 and B5 are 0, 5, 10, 20, 40 and 80 t ha^{-1} , respectively.

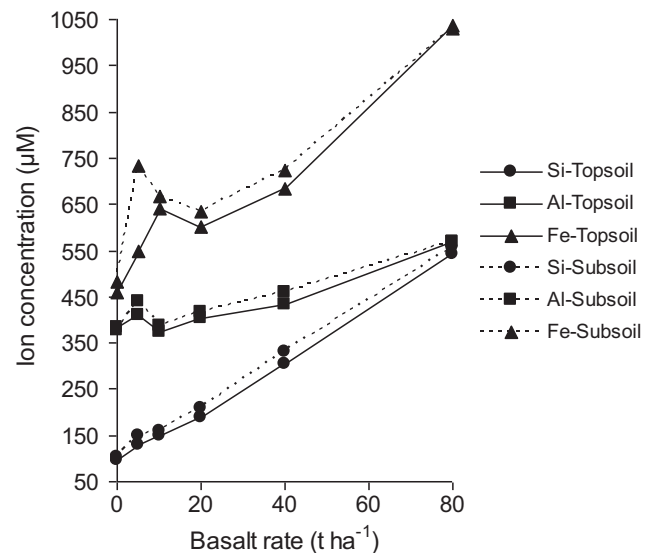


Fig. 4. The effect of basalt incubation on amorphous material formation in the topsoil (solid) and subsoil (dash) after 18 month. Note: Rates of 0, 5, 10, 20, 40 and 80 t ha^{-1} , correspond to B0, B1, B2, B3, B4 and B5 symbols, respectively.

Table 2

Changes of PZNC and positive charge, total negative and net charge as affected by basalt incubation determined at natural soil pH over 24-month incubation period.

Basalt Rate	Month 12					Month 24				
	PZNC	CEC _B cmol _c kg ⁻¹	AEC	CEC _T	N _{et} C	PZNC	CEC _B cmol _c kg ⁻¹	AEC	CEC _T	N _{et} C
<i>Topsoil</i>										
B0	3.05	3.1	2.1	3.6	-1.5	2.80	3.0	2.2	3.8	-1.6
B1	3.20	3.8	2.2	4.2	-2.0	2.60	5.4	0.6	5.8	-5.2
B2	2.95	4.2	2.2	4.4	-2.2	2.65	5.7	0.6	5.9	-5.3
B3	2.85	4.9	2.1	5.1	-3.0	2.62	7.7	0.6	7.8	-7.2
B4	2.70	6.2	1.7	6.4	-4.7	2.55	10.2	1.8	10.3	-8.5
B5	2.52	8.1	1.8	8.1	-6.3	2.50	11.8	1.8	11.9	-10.1
<i>Subsoil</i>										
B0	3.60	3.1	2.3	3.6	-1.3	2.90	3.1	2.4	3.9	-1.5
B1	3.20	3.8	2.1	4.1	-2.0	2.65	5.1	2.5	5.6	-3.1
B2	3.22	4.2	2.4	4.3	-1.9	2.70	5.5	2.1	5.8	-3.7
B3	2.95	5.0	2.2	5.2	-3.0	2.60	7.0	2.6	7.2	-4.6
B4	2.55	6.2	2.0	6.4	-4.4	2.55	8.3	2.2	8.5	-6.3
B5	2.55	7.3	1.8	7.4	-5.6	2.48	10.6	1.5	10.7	-9.2

CEC_B = negative charge for base cation (Ca adsorbed); AEC = positive charge (Cl adsorbed).CEC_T = Total negative charge (Ca + Al adsorbed).N_{et}C = net charge (AEC - CEC_T).Note: B0, B1, B2, B3, B4 and B5 are 0, 5, 10, 20, 40 and 80 t ha⁻¹, respectively.

was able to generate negative charge and its magnitude was controlled by basalt rates and the length of incubation periods.

The magnitude of surface negative charge and positive charge generation was assessed both at various equilibrium pH values and at natural soil pH. At equilibrium pH values, i.e., different basalt rates given a

similar equilibrium pH values (span from 3.0 to 5.0), the CEC_T as measured by amounts of Ca + Al adsorbed consistently increased with increasing basalt rates at any given equilibrium pH value (Fig. 5). In addition, the increase in incubation periods from month 12 to 24 further enhanced the CEC_T value, indicating that basalt has the potential to

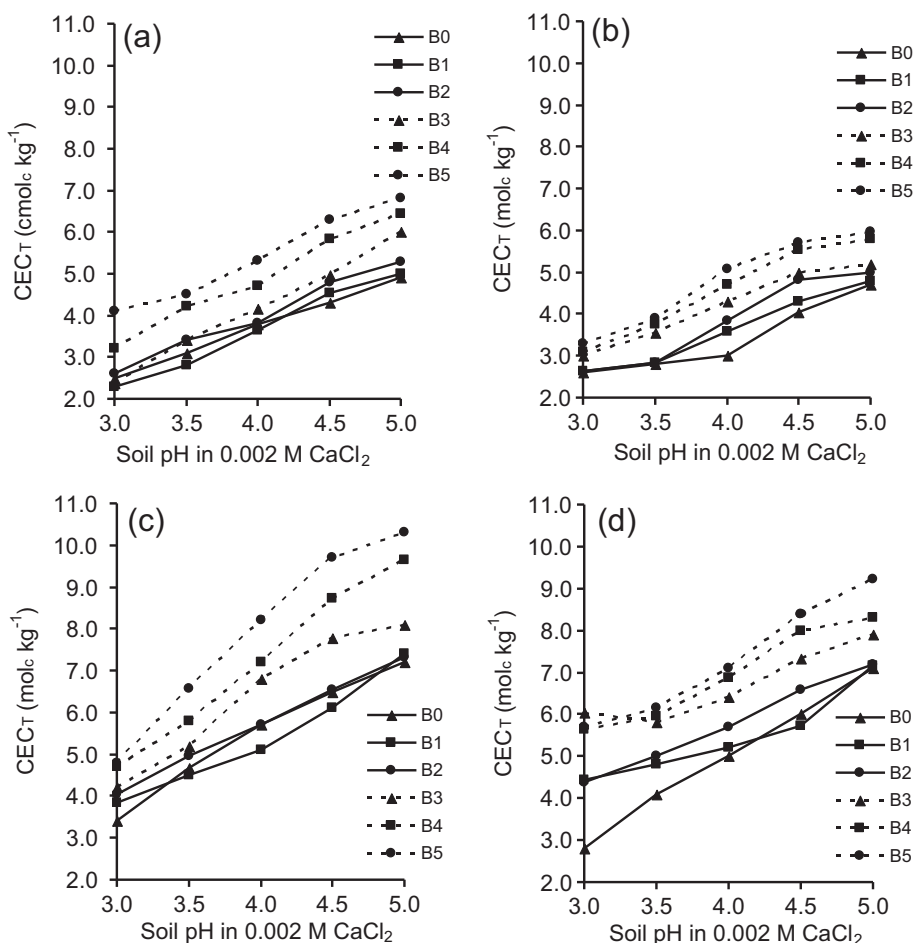


Fig. 5. CEC_T of equilibrium soil pH values (span from 3.0 to 5.0) at different basalt rates over an incubation period of 24 months: (a) topsoil month 12, (b) subsoil month 12, (c) topsoil month 24 and (d) subsoil month 24. Note: B0, B1, B2, B3, B4 and B5 are 0, 5, 10, 20, 40 and 80 t ha⁻¹, respectively.

improve electrochemical properties of the chemically degraded Oxisol for a longer period of time. For the topsoil, values of CEC_T increased from 2.4–4.7 to 4.0–6.8 $cmol_c\ kg^{-1}$, depending on basalt rates for month 12 and from 3.3–7.1 to 5.5–10.3 $cmol_c\ kg^{-1}$ for month 24. Corresponding values for subsoil were from 2.6–4.7 to 3.1–6.0 $cmol_c\ kg^{-1}$ for month 12 and from 2.6–7.1 to 6.5–9.2 $cmol_c\ kg^{-1}$ for month 24. This suggests that the increase in generation of negative charge of Oxisols was ascribed by the increase in basalt rates, pH values and length of incubation period. Calculation of net negative charge ($N_{et}C$), i.e. the amount of CEC_T subtracted by amount of positive charge, showed the magnitude increased from 0.0–2.6 to 2.0–5.1 $cmol_c\ kg^{-1}$ for topsoil and from 0.0–2.6 to 0.45–4.1 $cmol_c\ kg^{-1}$ for subsoil at month 12. The corresponding $N_{et}C$ values for month 24 increased from 1.0–6.3 to 3.2–8.7 $cmol_c\ kg^{-1}$ for topsoil and 0.05–5.0 to 4.2–7.6 $cmol_c\ kg^{-1}$ for subsoil.

At natural soil pH (without changing soil pH by equilibrium), basalt incubation consistently increased CEC_T and net charge ($N_{et}C$) values with increasing basalt rates and incubation periods (Table 2). This observation agrees well with the observation of CEC_T values measured at equilibrium soil pH values. In the topsoil for month 12, the CEC_T and $N_{et}C$ values increased from 3.6 to 8.1 $cmol_c\ kg^{-1}$ and from 1.5 to 6.3 $cmol_c\ kg^{-1}$, respectively, depending on the basalt rates. The corresponding values for month 24 were from 3.8 to 11.9 $cmol_c\ kg^{-1}$ for CEC_T and 1.6–10.1 $cmol_c\ kg^{-1}$ for $N_{et}C$. Relatively similar trends and magnitudes of negative charge generation were observed for the subsoil at any corresponding basalt rate and incubation period. For example at month 24, the values of CEC_T and $N_{et}C$ were 3.9–10.7 $cmol_c\ kg^{-1}$ and 1.5–9.2 $cmol_c\ kg^{-1}$, respectively. Based on findings from the magnitude of negative charge generation attributed basalt incubation as measured under both equilibrium soil pH and natural soil pH conditions we

confirmed that basalt is a suitable material to be used to restore negative charge of either normal (represented by topsoil) or severely eroded Oxisols (represented by subsoil).

The effect of basalt incubation on surface positive charge (AEC) at natural soil pH values showed a decrease in value at the highest rates (40–80 $t\ ha^{-1}$) for month 12 and all rates for month 24 for the topsoil (Table 2). For the subsoil, only incubation rates at 80 $t\ ha^{-1}$ (B5) clearly decreased AEC values compared to the control treatment at all incubation periods. The decrease in AEC values indicated that basalt applied at a high rate may be masking the positive charge of colloidal surfaces. In addition, there is no evidence for generation of positive charge attributed to basalt incubation.

The proportion of CEC_T occupied by base cations consistently increased with increasing basalt rates and that magnitude increased with incubation periods from month 12 to 24 (Table 2). This is in contrast to the proportion of CEC_T occupied by acidic cation (Al) that increased with decreasing basal rates. Interestingly, the values of CEC_T and CEC_B were comparable at basalt rates $\geq 10\ ha^{-1}$ (B2–B5) for all incubation periods, showing that the reserve acidity (Al) was almost entirely displaced by base cations from the exchange sites of soil colloids. This is particularly beneficial in management of highly weathered soils (such as Oxisols) having agronomic significance. In all cases, the net negative charge generation was higher in the topsoil than the subsoil and the magnitude was higher for a longer period of incubation time. This indicates basalt continuously generate soil negative charge with increasing incubation time and has a longer residue effect.

An attempt was made to estimate the amount of CEC_B resulting from basalt by plotting the CEC_B values against basalt rates (Fig. 6). It is obvious from regression equations that for the topsoil every 10 $t\ ha^{-1}$ basalt rate increased CEC_B value of 0.6 and 0.9 $cmol_c\ kg^{-1}$ for months 12 and

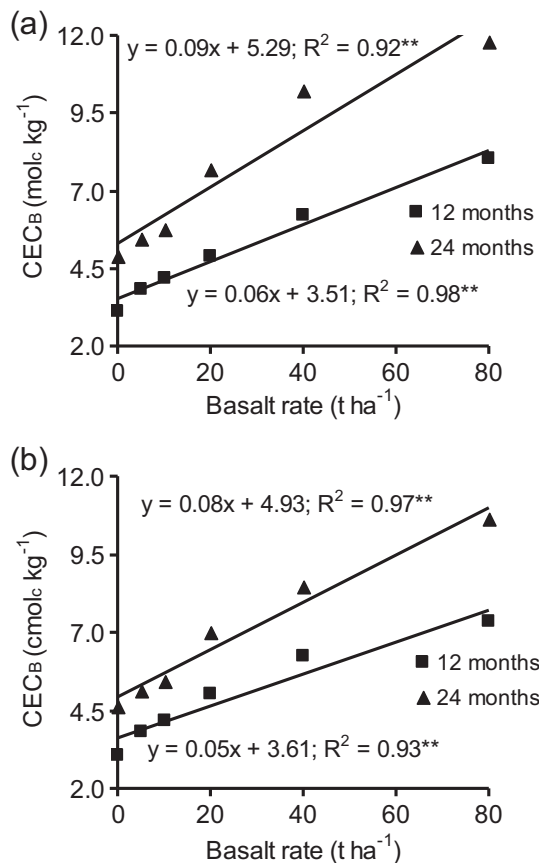


Fig. 6. Relationship between CEC_B and basalt rate over an incubation period of 24 months: (a) topsoil and (b) subsoil. Note: Rates of 0, 5, 10, 20, 40 and 80 $t\ ha^{-1}$, correspond to B0, B1, B2, B3, B4 and B5 symbols, respectively.

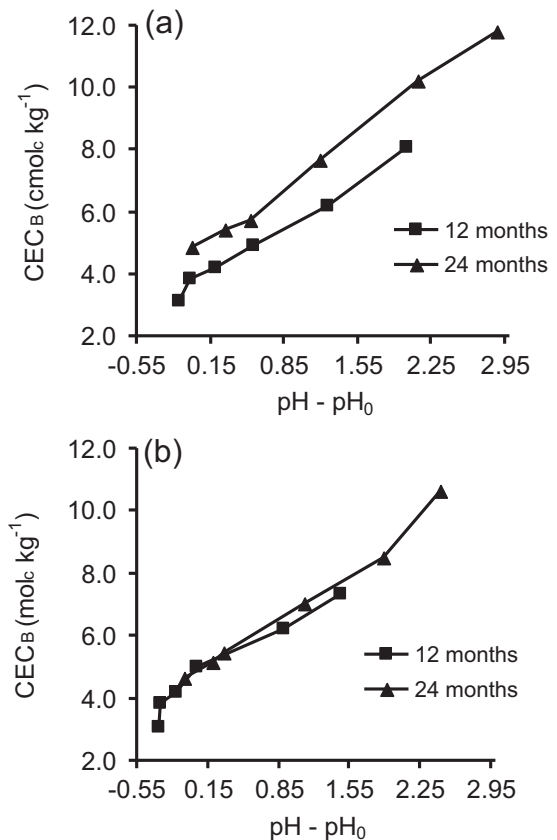


Fig. 7. The plot of CEC_B against delta pH: (a) topsoil and (b) subsoil. Note: Data points showed the increased basalt rate from left to right.

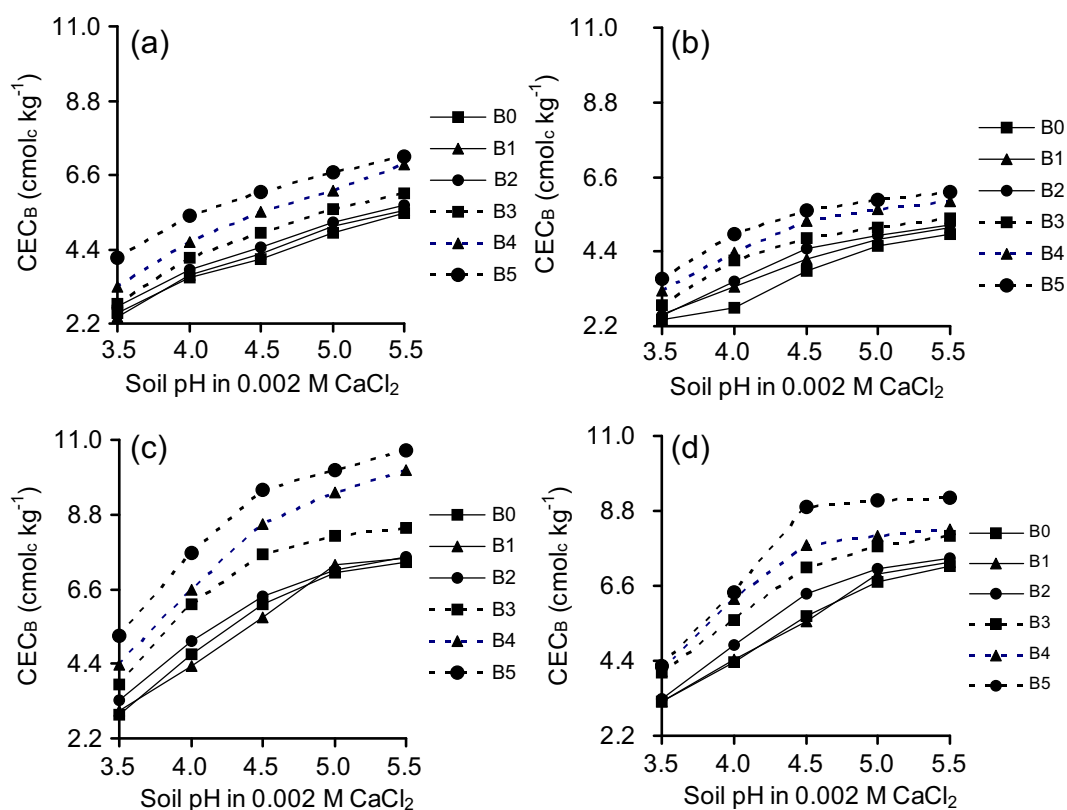


Fig. 8. CEC_B of equilibrium soil pH values (span from 3.5 to 5.5) at different basalt rates over an incubation period of 24 months: (a) topsoil month 12, (b) subsoil month 12 (c) topsoil month 24 and (d) subsoil month 24. Note: B0, B1, B2, B3, B4 and B5 are 0, 5, 10, 20, 40 and 80 $t\ ha^{-1}$, respectively.

24, respectively. The corresponding CEC_B values for the subsoil were 0.5 and 0.8 $cmol_c\ kg^{-1}$, respectively.

Factors affecting charge generation were further assessed by plotting CEC_B value against both $pH-pH_0$ and basalt rates. Results showed that the CEC_B value increased as the difference between soil pH and pH_0 values increased (Fig. 7). This indicated that the surface charge for variable charge components is actually dependent upon ($pH-pH_0$). Further examination of the data raised the question of whether the charge generation was entirely dependent upon $pH-pH_0$ or not for each soil layer. If the charge is entirely dependent upon $pH-pH_0$ difference, then all of the data should fall on a single curve when CEC_B is plotted against $pH-pH_0$ for two different periods. In fact, this is not the case; hence, other factors such as the increase incubation period of time also account for the increase in surface charge generation. Other factors were assessed by adjusting pH of the soils, receiving different basalt rates, to a similar equilibrium value (ranged from 3.5 to 5.5) and plotted against CEC_B (Fig. 8). If the increase in CEC_B value was solely controlled by increasing soil pH values, then all data of basalt rates will fall on the single curve within the range of pH observed. This did not happen. Instead, at any given similar equilibrium pH value, the higher the basalt rate the higher the CEC_B value. This finding convincingly confirms that every increment of basalt applied would generate “new negative sites” to retain cations in both topsoil and subsoil. The magnitude of this new negative sites increased with increasing incubation periods from month 12 to month 24 (e.g. Fig. 8a vs. 8c for a topsoil), again suggesting that the charge generation is a slow process, which leads to a longer residual effect of basalt. Hence basalt rate and incubation period, in addition to soil pH, contributed to the enhancement of CEC_B value. This implies that basalt is able to increase soil capacity to retain cations, has long residual effects and provides beneficial impact in managing the highly weathered soils.

3.4. Release of exchangeable cations from basalt

Results of statistical analyses of exchangeable Ca, Mg, K and Na released from basalts at different sampling periods within 24 month incubation are summarized in Table 3. Incubation of soils with basalt significantly increased concentrations of Ca, Mg, K and Na. However, there was no significant effect of interactions between basalt treatments and soil layers on exchangeable cations, except for K at month 12 and Na at months 12 and 24. The proportion of cations occupied exchangeable sites at any basalt rate and incubation period was in the order of

Table 3
Summary of statistical analysis of exchangeable cations released from basalt.

Treatment	Exchangeable cations			
	Ca	Mg	Na	K
Month 12				
Soil (S)	***	ns	ns	***
Basalt (B)	***	***	***	***
S*B	ns	ns	*	*
Month 18				
Soil (S)	*	ns	ns	***
Basalt (B)	***	***	***	***
S*B	ns	ns	ns	ns
Month 24				
Soil (S)	**	ns	ns	***
Basalt (B)	***	***	***	***
S*B	ns	ns	*	ns

Note: ns = $P > 0.05$; * = $P < 0.05$; ** = $P < 0.01$; *** = $P < 0.0001$.

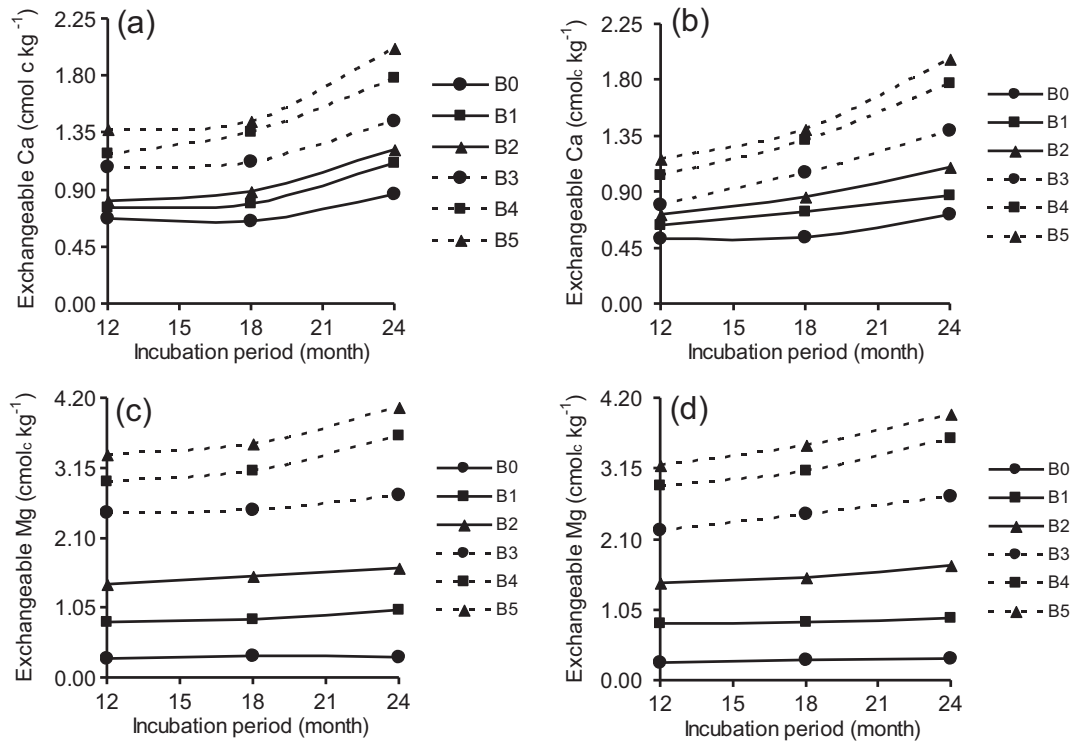


Fig. 9. Effect of basalt incubation on soil exchangeable Ca and Mg over a period of 24 months: (a) Ca-topsoil, (b) Ca-subsoil; (c) Mg-topsoil, (d) Mg-subsoil; Note: B0, B1, B2, B3, B4 and B5 are 0, 5, 10, 20, 40 and 80 t ha⁻¹, respectively.

decreasing magnitude $Mg > Ca > K > Na$ (Figs. 9 and 10). Every basalt rate increment consistently increased Ca, Mg, K and Na contents. Generally, the trend of individual cation increased from month 12 to months 18 and 24. The trend seems to still increase after 24 months, especially at the rates of more than 20 t ha⁻¹. Therefore, it is reasonable to expect much longer residual effect (more than 24 months) of basalt in increasing content of various cations of the chemically degraded Oxisol.

Table 4
Sum of exchangeable cations released from basalt with and without alcohol washings over a 24 month period at soil pH.

Treatment	Washed with alcohol				Unwashed with alcohol	
	Month 12		Month 24		Month 12	
	\sum cation [†]	BS [‡]	\sum cation	BS	\sum cation	BS
	cmol _c kg ⁻¹	%		%	cmol _c kg ⁻¹	%
<i>Topsoil</i>						
B0	1.4	45.7	1.7	57.0	1.8	59.6
B1	2.1	54.7	2.8	52.7	2.7	72.0
B2	2.8	67.0	3.7	64.6	3.6	85.3
B3	4.2	86.6	5.1	66.3	5.1	104.2
B4	4.9	79.4	6.5	64.1	6.4	104.0
B5	5.7	69.8	7.6	64.2	7.9	97.7
<i>Subsoil</i>						
B0	1.0	33.4	1.4	45.6	1.6	52.0
B1	1.9	48.9	2.3	45.5	2.4	63.1
B2	2.6	62.4	3.5	63.1	3.2	76.3
B3	3.7	73.1	4.9	70.2	4.7	94.7
B4	4.6	74.9	6.3	75.9	6.2	99.3
B5	5.3	72.7	7.2	67.9	7.5	102.4

[†] \sum cation = (Ca + Mg + K + Na).

[‡] BS = base saturation (sum cations[†]100/CEC_B).

If the surface negative charge at soil pH has been correctly estimated over the entire range of basalt incubation, then it has to be balanced by equivalent amount of exchangeable cations. Unexpectedly, the magnitude of the sum of exchangeable cations at months 12 and 24 was considerably lower than CEC_B measurements, suggesting insufficient amounts of exchangeable cations to balance the negative charge surfaces (Table 4). Calculation of base saturation showed only about 46–87% of surface negative charges (CEC_B) were balanced by exchangeable bases released from basalt. The low sum of base cations could be due to soil which was pre-washed with alcohol prior to extraction of exchangeable cations; the aim was to distinguish base cations in a soluble form (measured from soil solution) from exchangeable cations on exchange sites. Alcohol washing seems to reduce the dielectric constant of the liquid medium causing a reduction in surface negative charge and leads to some formerly exchangeable cations to be released and washed out. To support this statement, subsamples were analyzed for exchangeable cation at month 12 without alcohol pre-washing and the results have been inserted in Table 4 (right columns). It is readily shown that at high basalt incubation rates (≥ 20 t ha⁻¹), all negative charge sites were occupied by exchangeable cations, which were released by basalt dissolution, i.e., base saturation approximately 100%. However, for low incubation rates (≤ 10 t ha⁻¹), the sum of base cations was less than CEC_B values due to the soil being so degraded that even some of the CEC_B is still occupied by acidic cations. The control soils (0 t ha⁻¹) have base saturation of 60 and 52 % for topsoil and subsoil, respectively. This implies that 40 and 48% of soil negative charge of topsoil and subsoil, respectively, were occupied by acidic cations.

3.5. Release of soluble ions from basalt

Results of statistical analyses of various soluble ions released from basalts at different sampling periods within 24 month incubation are summarized in Table 5. The magnitude of cation concentrations

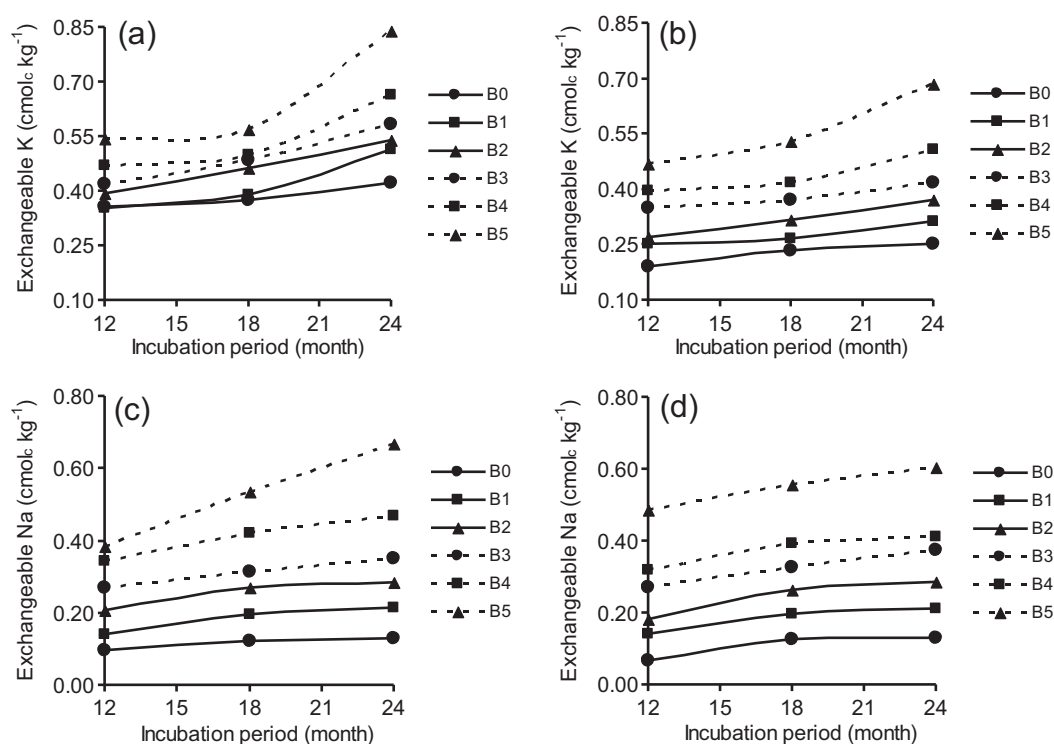


Fig. 10. Effect of basalt incubation on soil exchangeable K and Na over a period of 24 months: (a) K-topsoil, (b) K-subsoil; (c) Na-topsoil, (d) Na-subsoil; Note: B0, B1, B2, B3, B4 and B5 are 0, 5, 10, 20, 40 and 80 t ha⁻¹, respectively.

released into soil solution was determined by subtracting the control treatment from each basalt rate. The amount of cations (Ca, Mg, K, Na), and Si released from various basalt rates and that the suppression of Al and Mn in the soil solution at different incubation periods of topsoil and subsoil are shown in Figs. 11–13. These results indicate concentrations

of all cations (Mg, Ca, K, Na) and Si significantly increased for both the topsoil and subsoil and that their magnitude depended on basalt rates and incubation periods (Figs. 11 and 12). For example, basalt rates of 5–80 t ha⁻¹ and incubation periods of 9–24 months increased Mg concentrations of soil solution of topsoil, ranging from 36 to 590 μM at month 9 to 241 to 2958 μM at month 24.

The concentration of base cations in solution at any given incubation period is in the order of decreasing magnitude Na > Mg > Ca > K. This soluble cation order was different from exchangeable cations order (Mg > Ca > K > Na). This difference in order could be explained by competition of exchange sites by cations. Sodium is the monovalent cation and easy to be displaced by a higher valence of cations (Ca, Mg) from exchange sites, leading to the increase in Na concentration in the solution. The dominance of Mg on exchange sites was related to its high content (10.7%) among other cations in the basalt rock.

Concentration of soluble Si significantly increased with basalt rates. Different basalt rates showed no clear trend of differences in Si concentrations with incubation periods. The maximum Si concentration was achieved at incubation rate of 40 t ha⁻¹ from months 9 to 18, but shifted to incubation rate at 20 t ha⁻¹ for month 24 in all soil layers. It seems that the incubation rate at 80 t ha⁻¹ rapidly achieved saturation of Si in solution from month 9 to 24. Other rates (at 20 and 40 t ha⁻¹) achieved saturation at month 18 then the concentration decreased to month 24 (Fig. 11e and f) where the rate at 20 t ha⁻¹ gives the highest Si concentration. The decrease in Si with time at high incubation rates was probably due to the precipitation of Si in association with Al to form amorphous materials (Fig. 4), resulting the low concentration of Si in soil solution. According to Epstein (2001), when a soil solution is saturated with silicic acid, the amorphous rather than crystalline silica is formed. The silicic acid is adsorbed onto soil minerals and Si reacts with various aluminum compounds to form hydroxyl aluminosilicate (Exley, 1998; Wada, 1989), leading to a low concentration of silicic acid in soil solution

Table 5

Summary of statistical analysis of ions released from basalt into soil solution at various sampling periods over 24 months.

Treatment	Ca	Mg	Na	K	Si	Al	Mn	pH	EC
Month 9									
Soil (S)	ns	ns	ns	ns	***	***	nd	nd	ns
Basalt (B)	*	***	***	*	***	***	nd	nd	***
S*B	ns	ns	ns	ns	ns	***	nd	nd	*
Month 12									
Soil (S)	ns	ns	ns	ns	nd	***	***	ns	ns
Basalt (B)	***	***	***	***	nd	***	***	***	***
S*B	ns	**	ns	ns	nd	***	*	*	ns
Month 15									
Soil (S)	ns	ns	*	*	***	**	**	ns	ns
Basalt (B)	***	***	***	***	***	***	***	***	***
S*B	ns	ns	ns	ns	ns	***	**	ns	ns
Month 18									
Soil (S)	***	ns	ns	*	*	***	**	ns	ns
Basalt (B)	***	***	***	***	***	***	***	***	***
S*B	**	ns	ns	ns	ns	***	*	ns	ns
Month 24									
Soil (S)	***	ns	ns	ns	***	***	ns	ns	ns
Basalt (B)	***	***	***	***	***	***	***	***	***
S*B	ns	ns	ns	ns	ns	***	ns	ns	ns

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

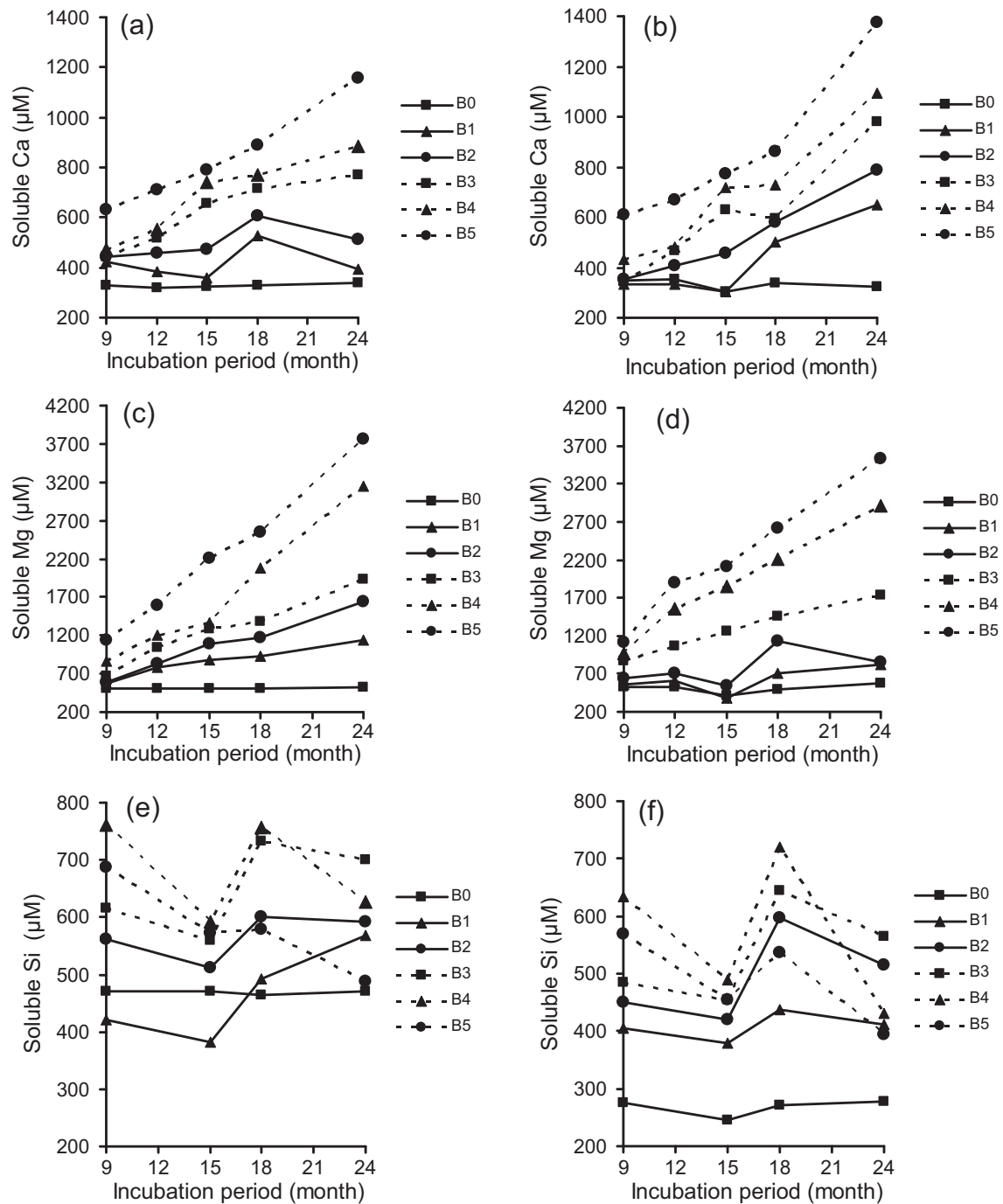


Fig. 11. The effect of basalt incubation on Ca, Mg and Si concentrations of soil solution over a period of 24 months: (a) Ca-topsoil, (b) Ca-subsoil, (c) Mg-topsoil, (d) Mg-subsoil, (e) Si-topsoil and (f) Si-subsoil. Note: B0, B1, B2, B3, B4 and B5 are 0, 5, 10, 20, 40 and 80 t ha⁻¹, respectively.

(Epstein, 2001). This is in agreement with the finding in this study for the basalt rate of $> 20 \text{ t ha}^{-1}$. The Si concentration in the present study increased from 250 to 759 μM for 20 t ha⁻¹; further increased to 80 t ha⁻¹ resulting in a decrease of Si concentration. The Si concentration in this study was higher than the common range after basalt incubation. The common range of Si concentration in soil solution is 0.1–0.6 mM, although both lower and higher values may be encountered (Epstein, 2001).

In contrast to Ca, Mg, K, Na and Si contents, the Al and Mn contents were reduced sharply both in the topsoil and subsoil (Fig. 13). Concentration of Al had been reduced from 41 to $< 9 \mu\text{M}$ for the topsoil and from

125 to $< 12 \mu\text{M}$ for the subsoil at basalt rate of 5 t ha⁻¹ and incubation period of 9 months (Fig. 13a). The concentration of Mn followed a similar trend to that of Al (Fig. 13b). In the topsoil, Mn concentration decreased from 203 to 43 μM and in the subsoil from 299 to 85 μM . Further increase in basalt rate up to 80 t ha⁻¹ could decrease Al and Mn concentrations to $< 5 \mu\text{M}$. It seems that the incubation rate of 5 t ha⁻¹ has sufficiently lower Al and Mn concentrations and their concentrations still remained low until the end of the incubation period (24 months). This suggests the residual effect of basalt even at low application rate may be effective in suppressing the toxic ions in Oxisols for at least two years.

Changes in pH and electrical conductivity (EC) of soil solution at various basalt rates and incubation periods are shown in Figs. 14 and 15. Basalt incubation showed significantly increased pH values of the soil solution at all incubation periods for both topsoil and subsoil. However, there were no significant interaction effects between basalt application and soil layers. In general, every basalt rate increment significantly increased pH values of the soil solution of the topsoil and subsoil. For example at month 18 for the topsoil, the pH values increased from 4.3 (B0 = control) to 5.0, 5.7, 6.0, 6.6 and 7.4 for 5, 10, 20, 40 and 80 t ha⁻¹ application rates, respectively. This indicates basalt was able to reduce the acidity of Oxisol soil solution even at the low application rate (B1, 5 t ha⁻¹).

The trend of incubation period effect from months 12 to 24 significantly decreased soil solution pH values, depending on basalt rates. The rates of 5–20 t ha⁻¹ (B1 to B3) showed the trend to regularly decrease with incubation periods from months 12 to 24. The effect of these basalt rates on soil solution significantly decreased at month 18 but pH values were still significantly higher than the control treatment at any corresponding incubation period. Further incubation to 24 month period showed there was no significant pH decrease at application rates > 10 t ha⁻¹. For soil incubation at 40 and 80 t ha⁻¹ (B4 to B5), soil solution pH values continuously increased to achieve maximum values of 7.0 and 7.5 for the topsoil and 6.7 and 7.3 for the subsoil, respectively at month 15; and these pH values decreased slightly at month 24. Findings in this study suggest that basalt residual effects of 5 t ha⁻¹ occurred until 18 months, whereas the rates at 10–80 t ha⁻¹ still remained high

at month 24, indicating a longer residual effect on soil solution pH, at least 24 months.

Electrical conductivity (EC) of the soil solution significantly increased with increasing basalt rates and incubation periods (Fig. 15). However, there were no significant effects of interaction between basalt rates with incubation periods and soil layers on EC values (Table 5). The EC values significantly increased at application rates ≥ 20 t ha⁻¹ but not for basalt application rates at ≤ 10 t ha⁻¹ during incubation from months 9 to 24. The increase in basalt rates from 20 to 80 t ha⁻¹ further significantly increased the EC value. The continued increase of EC with increasing basalt rates indicated that the basalt consistently released various ions into soil solution with the increase in magnitude with application rates. This agrees well with the increase concentrations of various ions (Ca, Mg, K, Na, Si) with basalt rates and incubation periods (Figs. 11 and 12).

The effect of incubation periods showed EC values were significantly higher at month 18 and 24 compared to incubation periods at months 9, 12 and 15. This suggests that the release of various ions from basalt takes place slowly, but the residual effect may occur for a longer period as shown by the EC values still linearly increased with increasing incubation periods where 91% of EC value was controlled by the longevity of basalt incubation as revealed by the determinant coefficients (R^2) of various applications rates. An exception was the topsoil where application rates of <10 t ha⁻¹ have R^2 less than 0.30. During the incubation periods from months 9 to 24, the EC increased from 0.57 to 2.08 mS/cm for the topsoil and from 0.49 to 2.21 mS/cm for the subsoil.

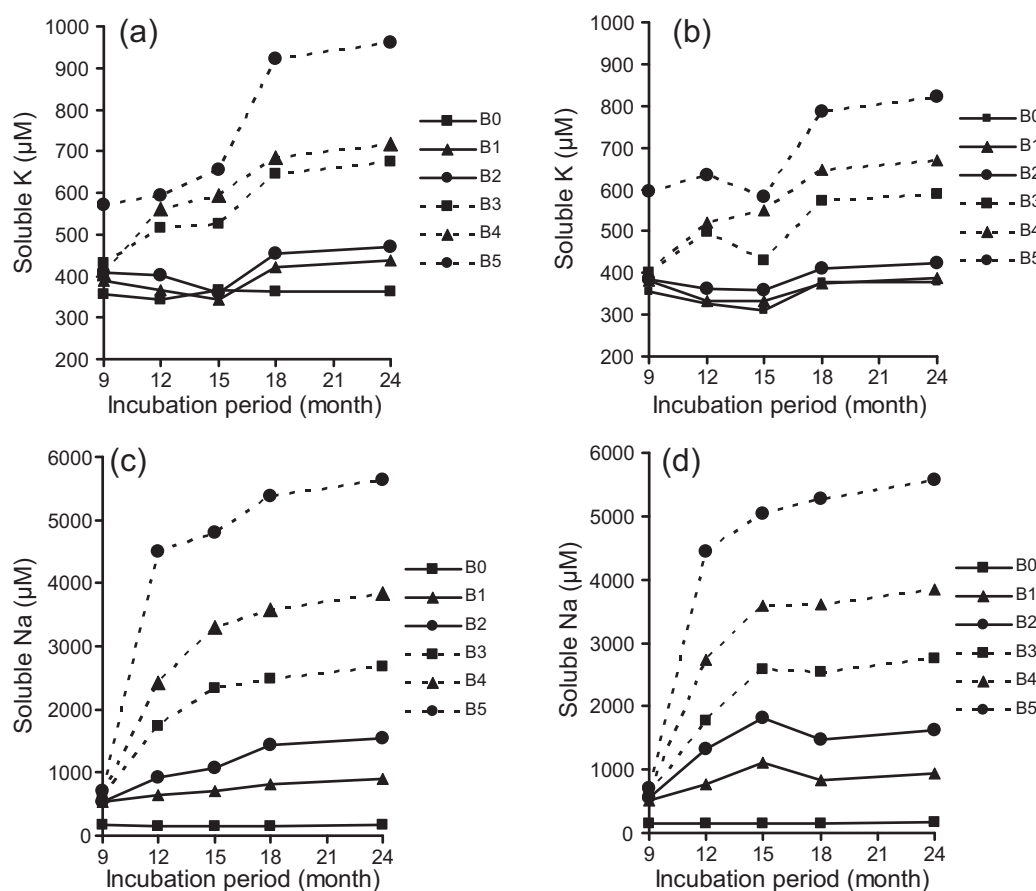


Fig. 12. The effect of basalt incubation on K and Na concentrations of soil solution over a period of 24 months: (a) K-topsoil, (b) K-subsoil, (c) Na-topsoil and (d) Na-subsoil. Note: B0, B1, B2, B3, B4 and B5 are 0, 5, 10, 20, 40 and 80 t ha⁻¹, respectively.

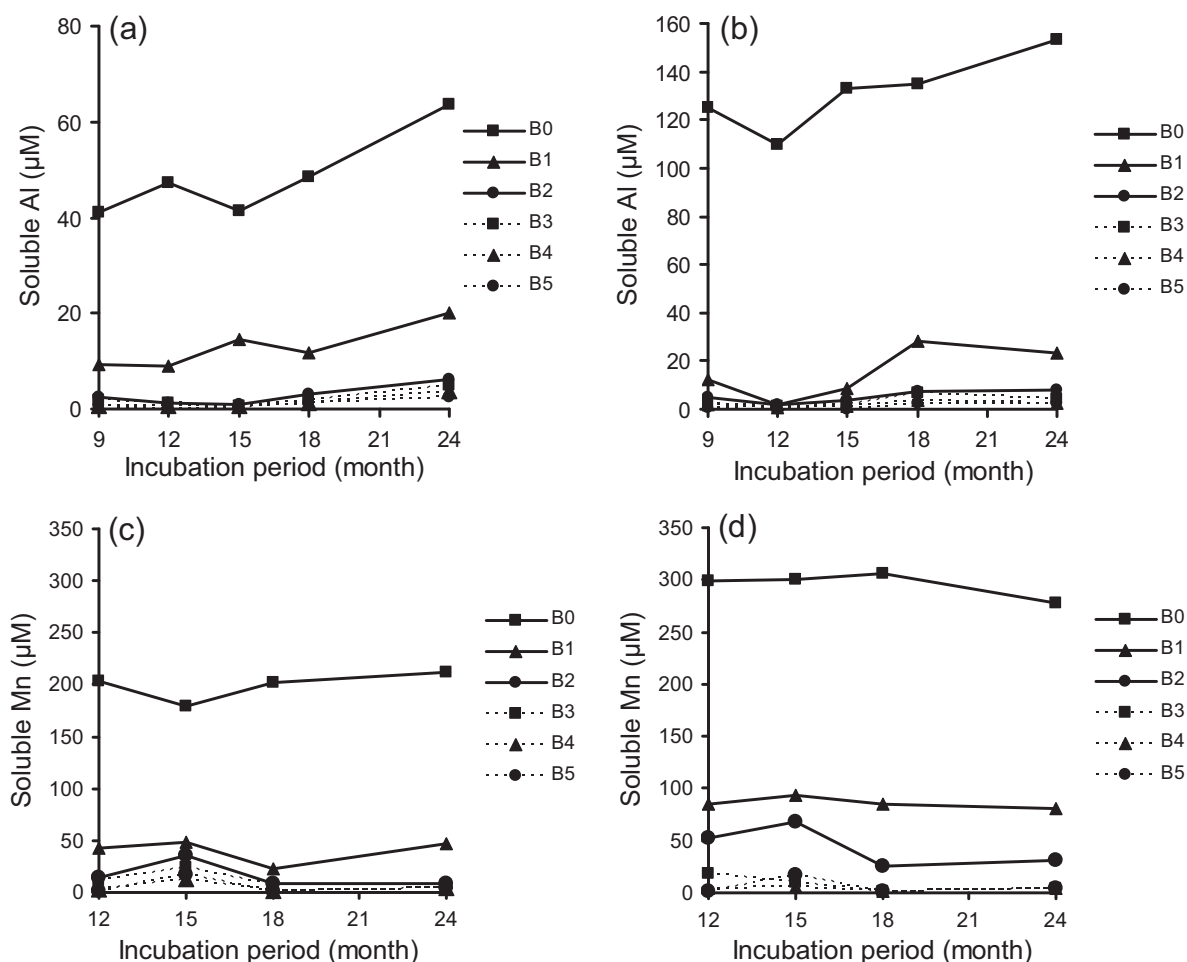


Fig. 13. The effect of basalt treatments on Al and Mn concentrations of soil solution: (a) Al-topsoil, (b) Al-subsoil, (c) Mn-topsoil and (d) Mn-subsoil. Note: B0, B1, B2, B3, B4 and B5 are 0, 5, 10, 20, 40 and 80 t ha⁻¹, respectively.

4. Conclusions

Incubation of an Oxisol with finely ground basalt of 0–80 t ha⁻¹ was able to increase soil pH from 3.9 to 6.5 for both topsoil and subsoil during 24 month. Basalt incubation at low rates (<10 t ha⁻¹) significantly increased soil pH and maintain it during 24 months, while at higher rates (>20 t ha⁻¹) soil pH increased to the end of experiment, suggesting a long residue effect.

Basalt incubation was able to improve soil charge characteristics by decreasing pH₀ and PZNC values, suggesting generation of negative charge. Increasing basalt rates at a given similar equilibrium pH value showed the CEC_B always increase with increasing basalt rates, indicating every increment of basalt rates would generate “new negative sites” to retain cations. The total net negative charge (N_{et}C) generation increased from 1.0–6.3 to 3.2–8.7 cmol_c kg⁻¹ for topsoil and from 0.05–5.0 to 4.2–7.6 cmol_c kg⁻¹ for subsoil.

The magnitude of charge measurement at natural soil pH, which is considered closely represent field condition, showed total negative charge (CEC_T) sharply increased from 3.8 to 11.9 cmol_c kg⁻¹ for topsoil and from 3.9 to 10.7 cmol_c kg⁻¹ for subsoil. The corresponding values for N_{et}C increased from 1.6 to 10.1 cmol_c kg⁻¹ for topsoil and from 1.5 to 9.2 cmol_c kg⁻¹ for subsoil.

Basalt incubation continuously released base cations as revealed by the significant increases in Ca, Mg, K and Na with time, both in the forms of exchangeable cations (measured from solid phase) and soluble

cations (measured from solution) with concomitant reduction in toxic Al and Mn. The magnitude of exchangeable cations, in order of decreasing content, was Mg > Ca > K > Na, while the order of soluble cations was Na > Mg > Ca > K.

Based on the findings from generation of soil negative charge, cations released from basalt and decreasing Al and Mn, it is suggested that finely ground basalt could be used to restore pH, CEC, exchangeable cations and soluble cations in order to increase productivity of either the normal or severely eroded Oxisols.

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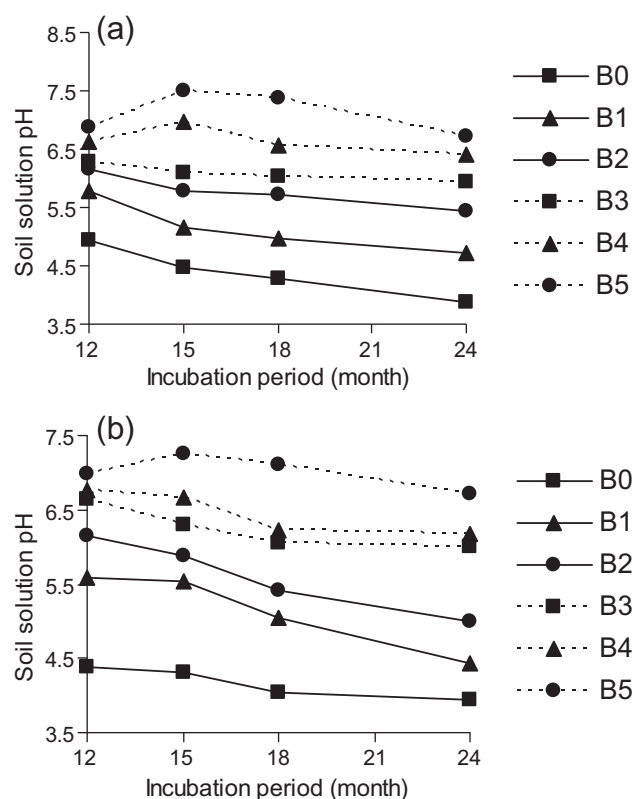


Fig. 14. The effect of basalt treatments on pH of soil solution: (a) topsoil and (b) subsoil. Note: B0, B1, B2, B3, B4 and B5 are 0, 5, 10, 20, 40 and 80 t ha⁻¹, respectively.

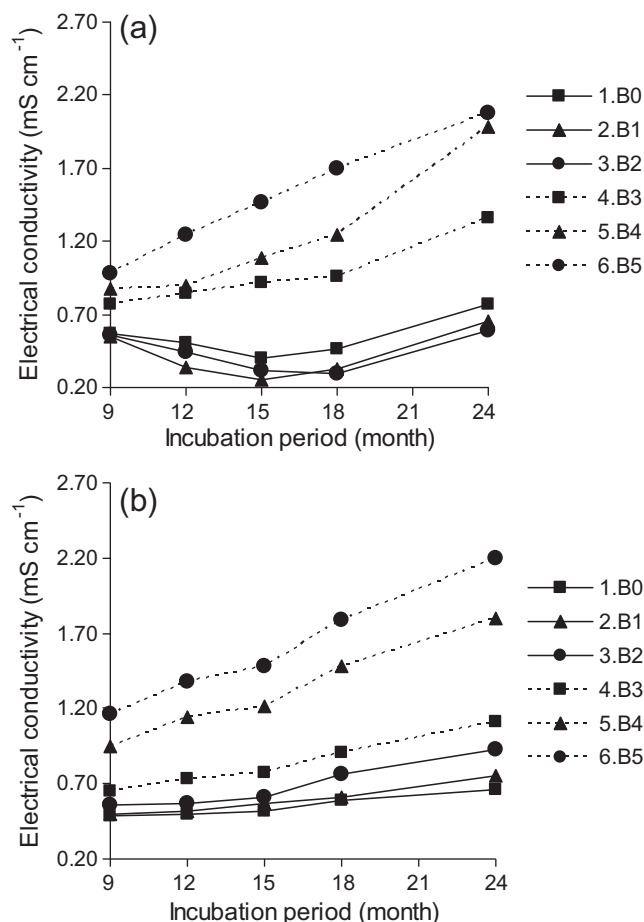


Fig. 15. The effect of basalt treatments on electrical conductivity of soil solution: (a) topsoil and (b) subsoil. Note: B0, B1, B2, B3, B4 and B5 are 0, 5, 10, 20, 40 and 80 t ha⁻¹, respectively.

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