



# 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<sup>-1</sup>) 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<sub>et</sub>C) from 0.0–6.3 to 3.2–8.7 cmol<sub>c</sub> kg<sup>-1</sup>, 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<sub>et</sub>C sharply increased from 1.5 to 10.1 cmol<sub>c</sub> kg<sup>-1</sup> after basalt application. The higher N<sub>et</sub>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<sub>T</sub>) values were comparable to the negative charge occupied by base cations (CEC<sub>B</sub>) at basalt incubation rates of ≥ 10 t ha<sup>-1</sup>, 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  $\mu\text{m}$ ) 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 charge 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; Herbillion, 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 ( $\text{H}^+$  and  $\text{OH}^-$ ) 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  $\text{H}^+$  and  $\text{OH}^-$ , 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 ( $N_{\text{et}}C$ ) 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  $\mu\text{m}$  (53%), 50–106  $\mu\text{m}$  (26%), 105–250  $\mu\text{m}$  (14%), 250–500  $\mu\text{m}$  (5%) and 500–2000  $\mu\text{m}$  (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%),  $\text{K}_2\text{O}$  (1.79%),  $\text{Na}_2\text{O}$  (2.59%),  $\text{SiO}_2$  (43.20%),  $\text{Al}_2\text{O}_3$  (12.90%),  $\text{Fe}_2\text{O}_3$  (12.90%),  $\text{P}_2\text{O}_5$  (0.77%), and  $\text{SO}_2$  (<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  $\text{t ha}^{-1}$ , 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  $\text{t ha}^{-1}$  and not in  $\text{g pot}^{-1}$ .

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

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