

**IMPROVEMENT OF CHARGE CHARACTERISTICS OF OXISOLS USING
BASALT AND RICE HUSK COMPOST FOR COCOA GROWTH**

By

MARKUS ANDA

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfilment of the Requirements for the Degree of Doctor of Philosophy**

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DEDICATION

**THIS THESIS IS DEDICATED TO MY BELOVED MOTHER, DEBORA LISUBUA,
AND TO THE MEMORY OF MY LATE FATHER, A.S. ANDA**

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in
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Chairman : Professor Shamsuddin Jusop, PhD

Faculty : Agriculture

One of the major limiting factors of Oxisols for agricultural crop production is a very low negative charge, leading to deficiency of base cations imparted by leaching. This condition is exacerbated by the low pH and high Al saturation. Basalt is naturally available and well known as parent material of fertile and highly productive soils, whereas rice husk is an agro-waste that can cause serious environmental problems, which on the other hand, is a highly valuable material if used as a soil amendment. The general objective of this study was to assess charge characteristics of Oxisols and restore their productivity by generating surface negative charge and increasing nutrient content using basalt and rice husk compost for cocoa growth.

Charge characteristics of three Oxisols were determined using potentiometric titration method. Results indicate that the B horizons of profile derived from basalt (Kuantan Series) had considerably lower pH_0 values (4.1-4.9) than those of the profiles derived from serpentinite (5.6-5.8) (Sungai Mas Series) and andesite (5.3-6.0) (Segamat Series). These high pH_0 values indicate the soils have very low negative charge. The removal of SOM or iron oxides increased or decreased pH_0 values, respectively, suggesting that SOM is responsible in lowering pH_0 values, while iron oxides in increasing pH_0 values.

The comparison of total SOC at corresponding application rates (0 to 20 t ha⁻¹) of

composted rice husk (CRH) under laboratory, glasshouse and field conditions for the first 12 months showed the magnitude of SOC content was in the order field > laboratory > glasshouse. The magnitude of SOC residual in soil was higher for the field conditions (0.24-0.69% C) than laboratory (0.05-0.23% C) and glasshouse (0.05-0.17% C) although the SOC loss was higher for the field (0.25-0.97 unit) than laboratory (0.04-0.16 unit) and glasshouse (0.04-0.22 unit). This is probably due to the interaction between CRH and *Gliricidia* litter to preserve organic C in the soils.

The type of organic C functional groups was determined using a solid state cross polarization magic angle spinning (CP/MAS) ^{13}C nuclear magnetic resonance (NMR) spectroscopy. The C functional groups were similar when determined under laboratory, glasshouse and field conditions. Under laboratory and glasshouse conditions, O-alkyl C was dominant, followed by acetal with minor proportion of alkyl, methoxyl, aromatic, phenolic and carboxyl C. For field conditions, the organic C functional groups were dominated by O-alkyl and alkyl C, followed by aromatic, carboxyl and acetal C.

The three decomposition indices: alkyl/O-alkyl C ratio (A/O-A), hydrophobicity/hydrophilicity ratio (HB/Hi) and aromaticity were related to the decrease in total SOC content and CO_2 production. The trends of the three indices in all conditions were similar, i.e., all values increased with increasing duration of CRH application, suggesting the increase of decomposition rate. The changes of decomposition indices within different periods for the first 12 months were very small in all conditions. These findings indicate CRH decomposed slowly; thereby it has a long residence time in soil.

Point of zero net charge (PZNC) was determined using ion adsorption method. Charge characteristics obtained at various sampling times within 24 months of

basalt application for laboratory and field conditions, and 15 months for glasshouse showed consistent decreases in pH_0 and PZNC values with time, but they decreased slowly, suggesting that the basalt was able to generate negative charge. However, the process took place rather slow. The exception was basalt application in the subsoil under laboratory conditions which increased pH_0 values.

The rates of basalt application for laboratory and glasshouse conditions were 0 to 80 t ha⁻¹, whereas for field conditions they were 0 to 20 t ha⁻¹. Hence, to indicate the generation of negative charge of the three conditions, application rates of 0 to 20 t ha⁻¹ and sampling time of month 12 were used (except for field 24 month was used). The net negative charge generation ($N_{et}C$) at equilibrium soil pH 5.0 was 1.5, 1.0 and 1.9 cmol_c kg⁻¹ for laboratory, glasshouse and field conditions, respectively. The corresponding $N_{et}C$ values under natural soil pH were 1.8, 0.3 and 2.0 cmol_c kg⁻¹. Further increase of application periods to 24 months and 15 months for laboratory and glasshouse, respectively increased $N_{et}C$ values by 3.5 and 0.6 cmol_c kg⁻¹, respectively. The application of basalt significantly increased Ca, Mg, K, Na and Si of the *in situ* soil solution. The concentration of base cations at any given incubation period under laboratory conditions is in the order of Na > Mg > Ca > K, suggesting that Na was released the fastest, followed by Mg, Ca and K. Under glasshouse and field conditions, the order of ion concentration is shifted to Mg > Ca > Na > K and Ca > Mg > Na ~ K, respectively.

For composted rice husk (CRH), the duration of application under laboratory, glasshouse and field conditions was similar to basalt. The CRH application of 0 to 20 t ha⁻¹ consistently decreased pH_0 and PZNC values in all conditions. In contrast to basalt, the CRH in the subsoil under laboratory conditions decreased pH_0 values. The $N_{et}C$ generation at equilibrium soil pH of 5.0 was 0.4, 0.6 and 2.3 cmol_c kg⁻¹ for laboratory, glasshouse and field conditions, respectively. The corresponding $N_{et}C$ values under natural soil pH were 0.5, 0.5 and 3.3 cmol_c kg⁻¹.

The application of CRH significantly increased concentrations of Ca, Mg, K, Na and Si of the *in situ* soil solution at application rate of 40 to 80 t ha⁻¹ under laboratory and at application rate of ≥ 10 t ha⁻¹ for glasshouse and field conditions. The order of released ions were K > Na > Si > Mg > Ca for laboratory, Si > K > Mg > Ca > Na for glasshouse and Si > Ca > K > Mg > Na for field conditions.

In contrast to K, Si, Mg, Na and Ca concentrations, the application of basalt or CRH and their combination significantly decreased concentrations of Mn and Al in all conditions.

The individual application of basalt and CRH significantly increased height, stem diameter and dry matter weight (DMW) of cocoa under glasshouse conditions. The cocoa growth significantly increased at application rates of ≥ 10 t ha⁻¹ for basalt and ≥ 20 t ha⁻¹ for CRH. The optimal rates of basalt and CRH under glasshouse conditions were 22 and 20 t ha⁻¹, respectively. The results from glasshouse (for CRH) were in agreement with the results from the field experiment. CRH in combination with basalt significantly increased the height and stem diameter of cocoa under field conditions. The application of 5 t ha⁻¹ is suggested for field application as this rate significantly increased cocoa growth compared to control but was not significantly different with 10 and 20 t ha⁻¹ application rates.

Basalt and rice husk could be used to restore chemical properties of Oxisols as they are able to increase soil negative charge, increase nutrient content of *in situ* soil solution and reduce Al and Mn, which in turn significantly improved cocoa growth.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**MEMPERTINGKATKAN CIRI-CIRI CAS TANAH *OXISOLS* MENGGUNAKAN
BASALT DAN KOMPOS SEKAM PADI UNTUK TUMBUHBESARAN KOKO**

Oleh

MARKUS ANDA

Disember 2006

Pengerusi : Profesor Shamsuddin Jusop, PhD

Fakulti : Pertanian

Satu daripada faktor utama yang menjadi limitasi pada tanah *Oxisol* untuk pengeluaran tanaman pertanian ialah cas negatif yang rendah sehingga mengakibatkan kekurangan kation-kation bes akibat daripada proses larutlesap. Keadaan ini lebih diperburukkan lagi oleh nilai pH yang rendah dan ketepuan Al yang tinggi. Basalt tersedia secara asli dan dikenalpasti sebagai bahan induk tanah yang subur dan berproduktif, manakala sekam padi pula merupakan bahan buangan pertanian yang boleh menimbulkan pencemaran alam sekitar tetapi bernilai tinggi jika digunakan sebagai pembaik tanah. Tujuan kajian ini ialah mengetahui ciri-ciri cas tanah *Oxisol* dan membaikpulih produktivitiya dengan menambah cas negatif dan meningkatkan kandungan nutrien dengan menggunakan basalt dan kompos sekam padi untuk tumbuhbesaran koko.

Ciri-ciri cas tiga tanah *Oxisol* ditentukan dengan menggunakan kaedah titratan potensiometrik. Keputusan menunjukkan profil tanah yang terjadi daripada basalt (Siri Kuantan) mempunyai nilai titik cas sifar (pH_0) lebih rendah (4.1-4.9) berbanding dengan pH_0 profil tanah yang terjadi daripada serpentinit (5.6-5.8) (Siri Sungai Mas) dan andesit (5.3-6.0) (Siri Segamat). Nilai pH_0 yang tinggi menunjukkan tanah mempunyai cas negatif sangat rendah. Pembuangan bahan organik dan oksida besi mengikut turutan meningkatkan atau menurunkan nilai pH_0 . Ini menunjukkan bahawa bahan organik bertanggung jawab keatas

penurunan pH_0 , manakala besi oksida untuk meningkatkan nilai pH_0 .

Perbandingan C organik total tanah (SOC) pada kadar aplikasi kompos sekam padi (CRH) yang sama (0 hingga 20 t ha^{-1}) di makmal, rumah kaca dan lapangan selepas 12 bulan menunjukkan magnitud SOC mengikut turutan lapangan>makmal>rumah kaca. Magnitud residu SOC adalah lebih tinggi daripada keadaan lapangan (0.24-0.69%C) berbanding keadaan makmal (0.05-0.23%C) dan rumah kaca (0.05-0.17%C) walaupun SOC yang hilang lebih tinggi pada keadaan lapangan. Hal ini mungkin disebabkan oleh interaksi antara CRH dengan serasah gliricidia untuk mengekalkan organik C dalam tanah.

Jenis kumpulan berfungsi organik C ditentukan dengan menggunakan keadaan pepejal pengutuban silang pengspinan sudut ajaib ^{13}C resonans magnet nucleus spektroskopi (CP/MAS ^{13}C NMR). Kumpulan C berfungsi yang diperolehi adalah sama pada keadaan makmal, rumah kaca dan lapangan. Pada keadaan makmal dan rumah kaca, O-alkil C adalah dominan, diikuti oleh asetal C dan sedikit alkil, metoksil, aromatik, fenolik dan karboksil C. Pada keadaan lapangan, kumpulan C berfungsi dikuasai oleh O-alkil dan alkil C, diikuti oleh aromatik, karboksil dan C asetal.

Tiga indeks pengurain iaitu nisbah alkil/O-alkil C (A/O-A), nisbah hidropobisiti/hidropilisiti (HB/HI), dan aromatisiti berkorelasi dengan penurunan SOC dan pengeluaran CO_2 . Tren ketiga indeks tersebut pada semua keadaan adalah sama iaitu semua nilai meningkat dengan pertambahan masa aplikasi CRH yang menunjukkan adanya peningkatan pereputan. Perubahan pereputan indeks pada masa berbeza selama 12 bulan adalah sangat kecil dalam semua keadaan. Bukti ini menunjukkan bahawa CRH lambat reput yang bermakna ia memberade lebih lama dalam tanah.

Titik cas net sifar (PZNC) ditentukan dengan menggunakan kaedah jerapan ion.

Ciri cas yang didapati pada masa persampelan yang berbeza selama 24 bulan basalt diaplikasikan pada keadaan makmal dan lapangan, dan, 15 bulan pada keadaan rumah kaca, menunjukkan penurunan nilai pH_0 dan PZNC secara konsisten dan perlahan dengan bertambahnya masa. Hal ini menunjukkan bahawa aplikasi basalt mampu menambah cas negatif. Walau bagaimanapun, prosesnya berjalan lambat, kecuali aplikasi basalt pada tanah bawah (subsoil) dalam keadaan makmal, meningkatkan nilai pH_0 .

Kadar aplikasi basalt pada keadaan makmal dan rumah kaca ialah 0 hingga $80t\ ha^{-1}$, manakala pada keadaan lapangan 0 hingga $20\ t\ ha^{-1}$. Oleh kerana itu aplikasi 0 hingga $20\ t\ ha^{-1}$ digunakan pada tiga keadaan dan masa persampelan 12 bulan kecuali keadaan dimana lapangan 24 bulan digunakan. Net cas negative ($N_{et}C$) yang diciptakan pada keseimbangan pH 5.0 masing-masing 1.5, 1.0 dan $1.9\ cmol_c\ kg^{-1}$ pada keadaan makmal, rumah kaca dan lapangan. Nilai $N_{et}C$ pada pH tanah semula jadi masing-masing 1.8, 0.3 dan $2.0\ cmol_c\ kg^{-1}$. Peningkatan masa aplikasi menjadi 24 bulan dalam makmal dan 15 bulan dalam rumah kaca dapat meningkatkan nilai $N_{et}C$ masing-masing kepada 3.5 dan $0.6\ cmol_c\ kg^{-1}$.

Aplikasi CRH pada keadaan makmal, rumah kaca dan lapangan menggunakan masa yang sama dengan percubaan basalt. Aplikasi CRH dari 0 hingga $20\ t\ ha^{-1}$ menurunkan nilai pH_0 and PZNC secara konsisten pada semua keadaan. Secara perbandingan dengan aplikasi basalt, aplikasi CRH pada subtanah dalam keadaan makmal menurunkan nilai pH_0 . $N_{et}C$ yang dikeluarkan pada keseimbangan pH 5.0 masing-masing ialah 0.4, 0.6 dan $2.3\ cmol_c\ kg^{-1}$ pada keadaan makmal, rumah kaca dan lapangan. Nilai $N_{et}C$ pada pH tanah asli masing-masing ialah 0.5, 0.5 dan $3.3\ cmol_c\ kg^{-1}$.

Aplikasi basalt dapat meningkatkan kandungan Ca, Mg, K, Na dan Si ke dalam larutan tanah secara nyata. Kepekatan bes kation pada masa eraman tanah dalam keadaan makmal ialah mengikut order $Na > Mg > Ca > K$. Hal ini menunjukkan bahawa

Na dilepaskan lebih cepat, diikuti oleh Mg, Ca dan K. Pada keadaan rumah kaca dan lapangan pelepasan bes kation ialah mengikut turutan $Mg > Ca > Na > K$ dan $Ca > Mg > Na \sim K$.

Aplikasi CRH dapat meningkatkan kandungan Ca, Mg, K, Na dan Si dalam larutan tanah secara nyata pada kadar 40 hingga 80 t ha⁻¹ pada keadaan makmal dan kadar ≥ 10 t ha⁻¹ pada keadaan rumah kaca dan lapangan. Kandungan ion ialah mengikut order $K > Na > Si > Mg > Ca$ pada keadaan makmal, $Si > K > Mg > Ca > Na$ pada keadaan rumah kaca dan $Si > Ca > K > Mg > Na$ pada keadaan lapangan.

Secara perbandingan dengan Ca, Mg, K, Na and Si, penggunaan basalt dan CRH secara bersendirian atau berkombinasi dapat menurunkan kepekatan Al dan Mn secara nyata dalam larutan tanah pada semua keadaan.

Aplikasi basalt dan CRH secara bersendirian atau berkombinasi dapat meningkatkan tinggi, diameter dan berat kering koko pada keadaan rumah kaca. Tumbesaran koko meningkat secara nyata pada kadar ≥ 10 t ha⁻¹ untuk basalt dan ≥ 20 t ha⁻¹ untuk CRH. Kadar optimal aplikasi basalt dan CRH adalah mengikut turutan 22 and 20 t ha⁻¹. Keputusan dari percubaan rumah kaca adalah selaras dengan keputusan keadaan lapangan. Kombinasi CRH dan basalt meningkatkan tinggi dan diameter koko secara nyata pada keadaan lapangan. Kadar 5 t ha⁻¹ disarankan untuk aplikasi basalt atau CRH kerana kadar tersebut nyata meningkatkan tumbesaran koko berbanding kawalan tetapi ianya tidak berbeza nyata dengan kadar 10 dan 20 t ha⁻¹.

Basalt dan CRH dapat digunakan untuk membaikpulih sifat kimia tanah *Oxisol* kerana kedua bahan tersebut dapat meningkatkan cas negatif, meningkatkan kandungan nutrien dalam larutan tanah dan mengurangi kandungan Al dan Mn. Ini menambahkan tumbesaran koko secara nyata.

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I certify that an Examination Committee has met on 4th December 2006 to conduct the final examination of Markus Anda on his Doctor of Philosophy thesis entitled "Improvement of charge characteristics of Oxisols using basalt and rice husk compost for cocoa growth" in accordance with Universiti Pertanian Malaysia (higher degree) Act 1980 and Universiti Pertanian Malaysia (higher degree) Regulations 1981. The committee recommends that the candidate be awarded the relevant degree. Members of the examination committee are as follows:

Anuar Abd. Rahim, PhD

Associate Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Chairman)

Rosenani Abu Bakar, PhD

Associate Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Member)

Hamdan Jol, PhD

Associate Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Member)

Karsutoshi Sakurai, PhD

Professor
Faculty of Agriculture
Kochi University
Japan
(Independent examiner)

HASANAH MOHD.GHAZALI, PhD

Professor/Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee are as follows:

Shamshuddin Jusop, PhD

Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Chairman)

Che Fauziah Ishak, PhD

Associate Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Member)

Syed Omar Syed Rastan, PhD

Associate Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Member)

AINI IDERIS, PhD
Professor/ Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 8 March 2007

DECLARATION

I hereby declare that the thesis is based on my original work except for the quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

MARKUS ANDA

Date: 31 January 2007

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