UNIVERSITI PUTRA MALAYSIA

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By

ROSAZLIN BINTI ABDULLAH

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

June 2013

DEDICATION

Dedicated to my parents, En. Abdullah Mohd Noh and Pn. Junidah Hamid, brothers and sisters who has been the pillars and inspirations of my life.

Abstract of thesis presented to the Senate of Universiti Putra
Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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Chairman : Assoc. Prof. Che Fauziah Ishak, PhD

Faculty : Agriculture

Recycled Paper Mill Sludges (RPMS) are complex mixtures of chemically recycled paper pulp, inorganic solid and chemical additives used in the paper manufacturing. These sludges are the final processed wastes from pulp and paper industries which are generated from different stages of papermaking. All paper industries produce sludge where disposal quantity is increasing every year which if not handled appropriately, led to environmental problem in the country. Since the usage of RPMS is restricted in Malaysia, studies on utilization of RPMS from Malaysian industries should be carried out to investigate the effect of RPMS on soil fertility, plant productivity and quality. The general objective of this study was to evaluate the effects of land application of raw and composted RPMS for agriculture and forestry applications in agroforestry system. Paper mill sludges have alkaline pHs ranging from 6.33 - 7.84 and thus can be important when utilized for acidic soil. Paper mill sludges contain total organic carbon ranging from 18.92 – 33.67% and organic matter content of 32.62 – 58.05% which can influence the biological, chemical and physical properties of soils. Paper mill sludges contain several essential plant

elements including N (0.31 – 4.05%), P (0.02 - 0.08%), K (0.02 - 0.42%), Ca (0.36 - 1.28%) and Mg (0.41- 1.06%). In general, the concentrations of heavy metals (Cd, Cu, Ni, Mn, Pb and Zn) in the paper mill sludges did not exceed Class 2 of the categories proposed by British Columbia Pulp and Paper Association (2000). The spectrum of ^{13}C NMR obtained in this study suggested that the RPMS exhibited peaks of cellulose and contains little lignin or hemicellulose like material. The FTIR spectrum complemented the structural information obtained in the ^{13}C NMR spectrum. Similarly, environmental contaminants of harmful chemicals such as dioxins/furans and PAHs should not be of concern in RPMS as the levels were negligible. Therefore, RPMS can be safely used as a fertilizer or soil amendment for land application. Recycled paper mill sludge mixed with EFB fibres at 1:1 ratio was recommended to be suitable for land application in agriculture and forestry. From this study, the compost can be used as potting media and as soil conditioner enriched with plant nutrients or as a soil amendment to improve the biological, chemical or physical properties of a soil. Based on the potentially mineralizable N contents, double the rates of recommended inorganic fertilizer (300 and 200 kg N-1 of raw and RPM compost, respectively) were suggested for land application of *Khaya senegalensis* and *Orthosiphon stamineus.* Application of raw and RPMS compost produced higher dry matter yield and growth performance than the control treatments for *Khaya senegalensis* and *Orthosiphon stamineus* for glasshouse and field condition and were comparable to the inorganic fertilizer treatments. Based on carbon fractionation study, results after 1 year duration indicated that utilization of RPMS as organic amendment onto soil produced higher C and N contents in free and occluded light fraction (F-LF and O-LF) and particulate organic matter (POM). Meanwhile, the paper mill sludge application has significantly reduced the soil bulk

density in the top soil which significantly affects the soil structure. However, the resonance peaks of any type of C structure in the soil remained completely unobservable even after removal of the magnetic materials followed by HF extraction. The FTIR spectra in soil at various time of sampling exhibited the same absorbance which indicates that no qualitative changes occurred during 6 months and 1 year of raw and RPMS compost application compared with the control treatments under glasshouse and field conditions. Total concentrations of Cu, Ni, Pb and Zn in soils were below the Investigation Level for Malaysian soils which the levels are taken at the 95th percentile of the heavy metals data for agricultural soils. Meanwhile, the concentrations of Cd are below the Australian Ecological Investigation Level (EILs) of 3 mg kg^{-1}. Concentrations of heavy metals in leaves were below the MPC value of the Malaysian Food Act 1983 and Food Regulation 1985. In the fractionation study, cadmium was dominant in the exchangeable fractions. Meanwhile, Cu, Ni, Mn, Pb and Zn occurred in the residual fraction. Application of raw and composted RPMS to soil showed an increase of concentration of Cu, Mn, Zn, Ni, Pb and As in the leachates at 15, 30, 60 and 120 cm soil depths compared to the control in the following order, NO_3^- > Zn > Mn > Cu > Ni > Pb > Cd. The concentration of NO_3^-, Cd, Cu, and Zn were below the established threshold value for drinking water by World Health Organization (WHO, 2008) guideline, which is the international guideline adopted by Malaysia. However, concentrations of Mn, Ni and Pb values were found to exceed the threshold value of WHO (2008) regulations. Therefore, heavy metals in the leachates need to be monitored until no more of these metals are released from the treated soil. This study indicated that using raw RPMS with addition of EFB (1:1) was able to improve the structure of raw RPMS as a compost product and potential

as organic fertilizer to substitute for the inorganic N fertilizer. Hopefully, this research can be used as preliminary information and reference on utilization of raw and RPMS compost as soil amendment for land application especially in Malaysia.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falfasah

KESAN APLIKASI BAHAN MENTAH DAN KOMPOS ENAPCEMAR KILANG KERTAS KITAR SEMULA KE ATAS TANAH, *Khaya senegalensis* DAN *Orthosiphon staminues*

Oleh

ROSAZLIN BINTI ABDULLAH

Jun 2013

Pengerusi : Prof. Madya Che Fauziah Ishak, PhD

Fakulti : Pertanian

Enap cemar kilang kertas kitar semula (RPMS) adalah campuran komplek kimia kertas kitar semula, pepejal takorganik dan bahan kimia tambahan yang digunakan dalam pemprosesan kertas kitar semula. Enap cemar ini adalah bahan buangan daripada proses akhir daripada industri pulpa dan kertas yang dihasilkan dari pelbagai peringkat pembuatan kertas. Semua industri kilang kertas menghasilkan enapcemar di mana kuantiti pelupusan semakin meningkat setiap tahun yang boleh membawa kepada masalah alam sekitar di negara ini jika tidak ditangani dengan baik. Oleh kerana penggunaan RPMS dikawal di Malaysia, maka kajian mengenai penggunaan RPMS daripada industri Malaysia perlu dijalankan untuk menyiasat kesan RPMS kepada kesuburan tanah, produktiviti dan kualiti tumbuhan. Objektif am kajian ini dijalankan untuk menilai kesan aplikasi bahan mentah dan kompos RPMS ke atas tanah untuk pertanian dan perhutanan di dalam system hutan tani. Enap cemar kilang kertas mempunyai pH alkali antara 6.33 - 7.84, di mana ianya penting jika digunakan pada tanah asid. Enap cemar kilang kertas mengandungi jumlah karbon organik antara 18.92 – 33.67 % dan kandungan bahan organik antara 32.62 -58. 05% yang mungkin menyebabkan perubahan kepada sifat biologi, kimia

dan fizikal tanah. Enap cemar kilang kertas mengandungi unsur-unsur yang diperlukan untuk tumbuhan termasuk N (0.31 - 4.05%), P (0.02 - 0.08%), K (0.02 - 0.42%), Ca (0.36 -1.28%) dan Mg (0.41 – 1.06%). Secara umum, kepekatan logam berat (Cd, Cu, Ni, Mn, Pb dan Zn) dalam enap cemar kilang kertas tidak melebihi Kelas 2 dalam pengelasan yang dicadangkan oleh Persatuan Pulpa dan Kertas British Columbia (2000). Spektrum ^{13}C NMR yang diperolehi dalam kajian ini mempamirkan bahawa RPMS terdiri daripada selulosa dan mengandungi sedikit lignin atau hemiselulosa. Spektrum FTIR melengkapi maklumat struktur yang diperolehi dalam spektrum NMR ^{13}C. Begitu juga, pencemaran alam sekitar bahan kimia berbahaya seperti dioksin / furan dan PAHs tidak harus menjadi kebimbangan dalam penggunaan RPMS kerana arasnya dalam RPMS adalah rendah. Daripada kajian ini, RPMS selamat diaplikasikan sebagai baja atau pemulih tanah untuk diaplikasikan ke atas tanah. Enap cemar kilang kertas yang dicampur dengan gentian tandan kosong kelapa sawit pada nisbah 1:1 (v/v) disyorkan sesuai untuk diaplikasikan ke atas tanah untuk pertanian dan perhutanan. Daripada kajian ini, kompos boleh digunakan sebagai media tanaman berpasu dan sebagai bahan penyubur tanah atau pemulih tanah untuk meningkatkan sifat biologi, kimia atau fizikal tanah. Berdasarkan potensi mineralisasi kandungan N, pada tahap dua kali ganda kadar baja takorganik (300 and 200 kg N^{-1} bahan mentah dan kompos RPMS) disyorkan untuk diaplikasikan ke atas tanah untuk *Khaya senegalensis* dan *Orthosiphon stamineus.* Aplikasi bahan mentah dan kompos RPMS memberikan hasil yang lebih tinggi dan meningkatkan pertumbuhan tanaman *Khaya senegalensis* dan *Orthosiphon staminues* untuk keadaan di rumah kaca dan di lapangan berbanding dengan kawalan dan setanding dengan baja takorganik. Berdasarkan pemeringkatan karbon selepas 1 tahun kajian, penggunaan RPMS sebagai pemulih

tanah menunjukkan peningkatan kandungan C dan N pada pemeringkatan pecahan bebas dan terperangkap (F-LF dan O-LF) dan zarah bahan organic (POM). Sementara itu, aplikasi bahan mentah dan kompos RPMS kilang kertas mengurangkan ketumpatan tanah yang memberi kesan ke atas struktur tanah. Walaubagaimanapun, tiada kehadiran resonan C dalam tanah walaupun selepas penyingkiran bahan magnet diikuti oleh pengekstrakan HF. Spektrum FTIR dalam tanah pada pelbagai peringkat persampelan menunjukkan bahawa tiada perubahan kualitatif berlaku selama 6 bulan dan 1 tahun oleh bahan mentah dan RPMS kompos berbanding kawalan pada pengeraman, rumah kaca dan kajian lapangan. Jumlah kepekatan Cu, Ni, Mn Pb dan Zn dalam tanah adalah di bawah paras penyiasatan untuk tanah di Malaysia yang merupakan tahap persentil ke-95 data logam berat untuk tanah pertanian. Sementara itu, kepekatan Cd adalah di bawah paras siasatan ekologi Australia (EILs). Kepekatan logam berat dalam daun Misai Kucing *(O.stamineus)* adalah di bawah tahap yang dibenarkan (MPC) oleh akta Makanan Malaysia 1983 dan Peraturan 1985. Dalam kajian pemeringkatan, kadmium adalah dominan dalam dalam bentuk tukarganti. Sementara itu, Cu, Ni, Mn, Pb dan Zn adalah dominan dalam bentuk sisa baki. Aplikasi bahan mentah dan kompos RPMS ke atas tanah menunjukkan peningkatan kepekatan NO_3^-, Cd, Cu, Mn, Ni, Pb dan Zn dalam air larutlesap pada kedalaman 15, 30, 60 dan 120 cm berbanding dengan kawalan dengan turutan berikut, NO_3^-, > Zn> Mn> Cu> Ni> Pb> Cd. Kepekatan NO_3^-, Cd, Cu, dan Zn adalah di bawah paras nilai garispaduan untuk air minuman oleh Pertubuhan Kesihatan Sedunia (WHO, 2008), di mana ia adalah garispanduan antarabangsa yang digunapakai oleh Malaysia. Walaubagaimanapun, kepekatan Mn, Ni, dan Pb di dapati melebihi daripada nilai garispanduan WHO (2008). Oleh itu, larutlesap logam berat hendaklah di beri perhatian sehingga tiada lagi logam yang

dilarutlesap dari tanah yang diberi rawatan. Kajian ini menunjukkan penggunaan bahan mentah RPMS dengan tambahan EFB (1:1) mampu memperbaiki struktur bahan mentah sebagai produk kompos dan berpotensi sebagai baja kimia untuk menggantikan baja N takorganik N. Adalah diharapkan agar kajian ini boleh membekalkan maklumat dan digunakan sebagai rujukan awal mengenai penggunaan bahan mentah dan kompos RPMS sebagai bahan pemulih untuk diaplikasikan ke atas tanah, terutamanya, di Malaysia.

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APPROVAL

I certify that a Thesis Examination Committee has met on 28 June 2013 to conduct the final examination of Rosazlin Binti Abdullah on her thesis entitled "Effects of Land Application of Raw and Composted Recycled Paper Mill Sludge on *Khaya Senegalensis* and *Orthosiphon Stamineus*" in accordance with the Universities and University College Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the student be awarded the Doctor of Philosophy.

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Date: 16 August 2013

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the Degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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Date:

DECLARATION

Declaration by graduate student

I hereby confirm that:

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