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ORGANIC AND MINERAL AMENDMENTS ON RICE (Oryza sativa L.) YIELD AND NUTRIENT RECOVERY EFFICIENCY

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By

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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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Faculty : Agriculture and Food Sciences (Bintulu)

Highly weathered soils such as Ultisols and Oxisols in Malaysia and elsewhere are low pH and nutrients but they are high in iron (Fe) and aluminium (Al). The high Fe and Al contents of these soils reduce their productivity. As a result, substantial amounts of fertilizers are used to sustain productivity of crops cultivated on Ultisols and Oxisols, especially those in the tropics. However, excessive use of chemical fertilizers degrades the environmental quality. To reverse this undesirable practice, amendments which are high in pH and cation exchange capacity such as crude humic substances, chicken litter biochar, and clinoptilolite zeolite could be exploited to improve soil chemical properties, lowland rice (cv. MR219) growth, nutrients uptake, nutrients recovery efficiency, and yield. River sand and the amendments were mixed at different rates to select the potential rice seeds germination medium. Crude humic substances, chicken litter biochar, and clinoptilolite zeolite at different rates were mixed with soil to determine their effects on ammonia volatilization, nutrients availability, nutrients (N, P, and K) adsorption and desorption capacity, pH buffering capacity, lowland rice growth, nutrients uptake, and nutrients recovery efficiency in laboratory, greenhouse, and field studies. Potential treatments of a greenhouse study were selected and further evaluated in field trials. Application of crude humic substances and chicken litter biochar did not minimize ammonia volatilization whereas, clinoptilolite zeolite reduced ammonia loss from urea under waterlogged condition. However, the three amendments improved soil pH and the availability of Ca, Mg, and Na in *Typic Paleudults* under laboratory condition. The organic amendments (crude humic substances and chicken litter biochar) increased soil total organic carbon, organic matter content, total N, and availability of K^+ and Mn^{2+}. Phosphorus availability was improved upon chicken litter biochar application whereas under laboratory condition, exchangeable ammonium increased with the application of clinoptilolite zeolite. Addition of crude humic substances reduced nutrients adsorption (N, P, and K) and K desorption rate however, they increased N and P desorption rate and pH buffering capacity. Chicken litter biochar increased N adsorption and pH buffering capacity but, it reduced P and K adsorption and so was N and P desorption rate. Lower N desorption rate with high N adsorption of the chicken litter biochar indicates the NH_4^+-N fixing capacity of this organic amendment. Clinoptilolite zeolite increased N and K adsorption, N desorption rate, and pH buffering capacity but, it reduced P adsorption and desorption rates of P

and K. Higher K adsorption with lower K desorption rate indicates that clinoptilolite zeolite has high affinity for K. Clinoptilolite zeolite (15%) mixed with sand (85%) was selected as germination medium for the greenhouse and field trials as it improved rice seedling shoot elongation. From the greenhouse study, crude humic substances at 5 t ha^{-1}, chicken litter biochar at 15 t ha^{-1}, and clinoptilolite zeolite at 15 t ha^{-1} were chosen for further field verification due to their potential to improve rice plant growth variables and selected soil chemical properties. Chicken litter biochar at 15 t ha^{-1} and crude humic substances at 5 t ha^{-1} increased MR219 rice yield by 88% and 38%, respectively in the first field trial. Reduced rates of crude humic substances (1.67 t ha^{-1}) and chicken litter biochar (5 t ha^{-1}) with reduction of chemical fertilizers by 37% increased rice yield by 57% and 75%, respectively in the second field trial. In the third field trial, the carryover effect of the chicken litter biochar on the rice yield was superior to those of crude humic substances, clinoptilolite zeolite, and the standard fertilization. Regardless of field trial, application of clinoptilolite zeolite had similar effect as normal fertilization on rice yield. Although, the conventional practice was profitable at the initial cycles, the profit associated with this practice decrease to loss by the third cycle. Rice farmers in Malaysia who patronize the conventional method are still surviving because of the Malaysian government subsidies on fertilizers, lime, and seeds. Irrespective of field trial, the use of crude humic substances was economically viable however, farmers can breakeven at second and third field cycles, respectively if they adopt chicken litter biochar and clinoptilolite zeolite in their farming practices. Incorporating crude humic substances or chicken littler biochar in the Malaysian rice cultivation is economically viable compared to the existing practice. It is recommended to produce biochar commercially in Malaysia from the agro industrial organic wastes or transfer technology to farmers to produce their own biochar to reduce the production cost. To refine this study, the organic and mineral amendments can be mixed to improve soil quality and rice yield. Apart from N, P, and K, other nutrients contribution to increase rice yield should be comprehensively studied in future studies.

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

PENAMBAH BAIK ORGANIK DAN MINERAL DALAM HASIL PADI (*Oryza sativa* L.) DAN KECEKAPAN PEMULIHAN NUTRIEN

Oleh

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Tanah yang sangat terluluhawa seperti *Ultisols* dan *Oxisols* di Malaysia dan di tempat lain mempunyai pH dan nutrien yang rendah tetapi ia tinggi dengan ferum (Fe) dan aluminium (Al). Kandungan Fe dan Al yang tinggi dalam tanah mengurangkan produktivitinya. Hasilnya, sejumlah besar baja digunakan untuk memampankan produktiviti tanaman yang ditanam pada *Ultisols* dan *Oxisols*, terutamanya di kawasan tropika. Walau bagaimanapun, penggunaan baja kimia yang berlebihan menggurangkan kualiti alam sekitar. Untuk menterbalikkan amalan yang tidak diingini ini, penambah baik yang tinggi dalam pH dan keupayaan pertukaran kation seperti bahan humik mentah, *biochar* tahi ayam, dan zeolit klinoptilolit boleh digunakan untuk meningkatkan sifat-sifat kimia tanah, pertumbuhan padi sawah (cv. MR219), pengambilan nutrien, kecekapan penggunaan nutrien, dan hasil. Pasir sungai dan bahan penambahan dicampur pada kadar yang berbeza bagi memilih medium percambahan benih yang berpotensi. Bahan-bahan humik mentah, *biochar* tahi ayam, dan zeolit klinoptilolit pada kadar yang berbeza telah dicampur dengan tanah untuk menentukan kesan penambahan tersebut terhadap pemeruapan ammonia, ketersediaan nutrien-nutrien, penjerapan dan penyahjerapan nutrien-nutrien (N, P, dan K), kapasiti keupayaan penampan pH, pertumbuhan padi tanah rendah, pengambilan nutrien, dan kecekapan penggunaan nutrien dalam kajian makmal, rumah hijau, dan lapangan. Rawatan yang berpotensi daripada kajian rumah hijau telah dipilih dan diniai secara lanjut dalam ujian lapangan. Penggunaan bahan humik mentah dan *biochar* tahi ayam tidak mengurangkan pemeruapan ammonia sedangkan, zeolit klinoptilolit mengurangkan kehilangan ammonia daripada urea di dalam keadaan bertakung air. Walau bagaimanapun, ketiga-tiga penambah baik telah meningkatkan pH tanah dan ketersediaan Ca, Mg, dan Na dalam *Typic Paleudults* di dalam keadaan makmal. Penambahan organik (bahan humik mentah dan *biochar* tahi ayam) meningkatkan jumlah karbon, kandungan bahan organik, jumlah N, dan ketersediaan K^+ dan Mn^{2+} tanah. Ketersediaan P meningkat apabila *biochar* tahi ayam digunakan sedangkan di dalam keadaan makmal, ammonium boleh tukar ganti meningkat dengan penggunaan zeolit klinoptilolit. Penambahan bahan humik mentah mengurangkan penjerapan (N, P, dan K) dan kadar penyahjerapan K bagaimanapun, ia meningkatkan kadar penyahjerapan N dan P, dan kapasiti keupayaan penampan pH. *Biochar* tahi ayam meningkatkan penjerapan N dan kapasiti keupayaan penampan pH tetapi, ia

mengurangkan penjerapan P dan K dengan kadar penyahjerapan N dan P. Kadar penyahjerapan N yang lebih rendah dengan penjerapan N yang tinggi pada *biochar* tahi ayam menunjukkan kapasiti pengikatan NH_4^+-N pada penambahan organik tersebut. Zeolit klinoptilolit meningkatkan penjerapan N dan K, kadar penyahjerapan N, dan kapasiti keupayaan penampan pH tetapi, ia mengurangkan penjerapan dan kadar penyahjerapan P dan K. Penjerapan K yang lebih tinggi dengan kadar penyahjerapan K yang lebih rendah menunjukkan bahawa zeolit klinoptilolit mempunyai tarikan yang tinggi untuk K. Zeolit klinoptilolit (15%) dicampur dengan pasir (85%) telah dipilih sebagai medium percambahan untuk percubaan-percubaan rumah hijau dan lapangan kerana ia meningkatkan pemanjangan pucuk anak benih padi. Daripada kajian rumah hijau, bahan-bahan humik mentah pada 5 t ha^{-1}, *biochar* tahi ayam pada 15 t ha^{-1}, dan zeolit klinoptilolit pada 15 t ha^{-1} telah dipilih untuk pengesahan lapangan seterusnya kerana potensi mereka untuk meningkatkan pembolehubah pertumbuhan tumbuhan padi dan sifat-sifat kimia tanah terpilih. *Biochar* tahi ayam pada 15 t ha^{-1} dan bahan humik mentah pada 5 t ha^{-1} meningkatkan hasil padi MR219 sebanyak 88% dan 38%, masing-masing dalam percubaan lapangan pertama. Kadar dikurang bahan humik mentah (1.67 t ha^{-1}) dan *biochar* tahi ayam (5 t ha^{-1}) dengan pengurangan baja kimia sebanyak 37% meningkatan hasil padi sebanyak 57% dan 75%, masing-masing dalam percubaan lapangan kedua. Dalam percubaan lapangan yang ketiga, kesan bawa ke depan *biochar* tahi ayam pada hasil padi adalah lebih tinggi daripada bahan humik mentah, zeolit klinoptilolit, dan pembajaan biasa. Tanpa mengira percubaan lapangan, penggunaan zeolit klinoptilolit mempunyai kesan yang sama seperti pembajaan normal pada hasil padi. Walaupun begitu, amalan konvensional adalah menguntungkan di awal kitaran penanaman, keuntungan daripada amalan ini akan berkurangan kepada kerugian pada kitaran yang ketiga. Pesawah di Malaysia yang mengamalkan kaedah konvensional masih mampu beroperasi kerana subsidi kerajaan Malaysia terhadap baja, kapur, dan biji benih. Tanpa mengira percubaan lapangan, penggunaan bahan humik mentah adalah berdaya maju kerana, petani boleh mendapat pulangan modal pada kitaran kedua dan ketiga masing-masing jika mereka mengamalkan penggunaan *biochar* tahi ayam dan zeolit klinoptilolit dalam amalan pertanian mereka. Penggunaan bahan humik mentah atau *biochar* tahi ayam biochar dalam penanaman padi di Malaysia adalah berdaya maju dari segi ekonomi berbanding dengan amalan yang sedia ada. Ia adalah disyorkan untuk menghasilkan *biochar* secara komersial di Malaysia daripada sisa-sisa organik industri agro atau pemindahan teknologi kepada petani untuk menghasilkan *biochar* mereka sendiri untuk mengurangkan kos pengeluaran. Untuk memperbaiki kajian ini, penambahan organik dan mineral boleh dicampur untuk meningkatkan kualiti tanah dan hasil padi. Selain daripada N, P, dan K, sumbangan nutrien-nutrien lain untuk meningkatkan hasil padi perlu dikaji secara menyeluruh dalam kajian pada masa depan.

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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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1/*n*	Freundlich adsorption isotherm constant related to adsorption condition
χ^2	Chi-square
AAS	Atomic Absorption Spectrophotometry
Al-P	Aluminium bound phosphorus
B_T	Temkin adsorption isotherm constant related to heat of sorption
Ca-P	Calcium bound phosphorus
C_e	Equilibrium concentration
CEC	Cation Exchange Capacity
Cv.	Cultivar
DAI	Days after incubation
DATP	Days after transplanting
EK	Exchangeable potassium
ERP	Egypt rock phosphate
FA	Fulvic acid
Fe-P	Iron bound phosphorus
FK	Fixed potassium
HA	Humic acid
K_F	Freundlich isotherm constant related to adsorption capacity
K_L	Langmuir isotherm constant related to bonding energy
K_T	Temkin isotherm equilibrium constant related maximum binding energy
NEK	Non-exchangeable potassium
OM	Organic matter
Pi	Inorganic phosphorus
Pocc	Occluded phosphorus
Pred	Reductant soluble phosphorus
Psol	Soluble and loosely phosphorus
q_e	Amount of adsorbate in the adsorbent at equilibrium
$q_{e,cal}$	Calculated values of adsorbate in the adsorbent at equilibrium from regression equation
$q_{e,meas}$	Measured values of adsorbate in the adsorbent at equilibrium from experimental
q_m	Maximum adsorption capacity
R^2	Coefficient of determination
rpm	Revolutions per minute
TOC	Total organic carbon
WSK	Water-soluble potassium

CHAPTER 1

INTRODUCTION

Rice (*Oryza sativa* L.) is one of the widely grown staple foods in the world. It is a very important food source in Asia including Malaysia. However, the self-sufficiency level for rice production in Malaysia is approximately 71.7 % (Siwar *et al*., 2014; Ministry of Agriculture and Agro-Based Industry, Malaysia, 2014). Moreover, the average rice production in Malaysia per hectare is approximately 4 t ha^{-1} which is lower than the potential rice yield of 10 t ha^{-1} (Omar, 2008; Siwar *et al*., 2014). This pressing issue calls for improvement in the existing rice production practices particularly in terms of efficient use of fertilizers and sustainable maintenance of soil productivity. This is essential because mineral soils of Malaysia such as Ultisols and Oxisols are highly weathered, acidic, and they are also inherently low in N, P, and K (Goh and Chew, 1995; Sallade and Sims, 1997; Zaharah *et al*., 1997).

The abundance of variable charge colloids in Ultisols and Oxisols as well as low pH and low cation exchange capacity (CEC) have led to the presence of large amounts of oxides and hydroxides of iron and aluminium in these soils. These oxides and hydroxides fix large amounts of soluble P resulting low concentrations of available phosphorus in soil solution (Wilson *et al*., 2004). Moreover, low soil CEC, high rainfall, and the hygroscopic and highly soluble properties of fertilizers cause significant reduction in nitrogenous, phosphatic, and potassic fertilizers use efficiency. Inefficient use of fertilizers by crops leads to nutrient deficiencies and yield reduction in rice (Goulding *et al*., 2008). To sustain the self-sufficiency level for rice production, fertilizer use has been emphasized. However, the demand for fertilizers in agriculture is associated with yearly increase in the price of the fertilizers (FAO, 2011). In addition, excessive use of fertilizers in rice production is not environmental friendly because this approach leads to environmental pollution such as ground water contamination, eutrophication of water bodies, and greenhouse gases emission (Daniel *et al*., 1998; Savci, 2012).

On the other hand, agricultural activities lead to production of substantial amount of wastes such as rice straw, rice husk, chicken litter, and sawdust. The production of rice and poultry in 2013 were 2.6 million metric tonnes and 1.3 million metric tonnes, respectively (Ministry of Agriculture and Agro-Based Industry, Malaysia, 2014). It has been estimated that approximately 1.3 million metric tonnes of rice straw are produced every year in Malaysia (Remli *et al*., 2014). On the average, 20% weight of paddy is husk (Kumar *et al*., 2012). This explains why approximately 0.5 million metric tonnes of rice husk was produced in Malaysia in 2013. For poultry waste, it has been estimated that a laying hen and broiler can produce about 138 g (25% dry substance) and 90 g (40% dry substance) of litter day^{-1}, respectively (Chun *et al*., 2015). Malaysia exported about 1.5 million meter cubes (m^3) of sawntimber from January to September 2015 (Malaysian Timber Industry Board, 2014). The sawdust waste production in sawmilling is about 8% of the total volume of timber input (Gan and Ho, 1995).

Agro-industrial wastes such as rice straw is usually burned *in situ* after harvest (Chen *et al*., 2008) whereas, sawdusts are burned under controlled condition in the mill or dumped. Because fresh chicken litter in agriculture has detrimental effects on humans and the environment, heating or composting is crucial to eliminate this problem (Chen and Jiang, 2014). Moreover, burning of agro-industrial or organic wastes release hazardous greenhouse gases and particles into the atmosphere. This causes numerous health and environmental problems (Chen *et al*., 2008; U.S.EPA, 2001).

To manage agro-industrial wastes sustainably, they can be transformed into beneficial amendments through composting and pyrolysis to produce compost, humic substances, and biochar. Production of the aforementioned organic amendments can minimize agro-industrial wastes disposal problems at the same time, the use of these amendments in agriculture also could mitigate nutrient leaching, ammonia volatilization, and P fixation problems in soils besides improving crop nutrients recovery efficiency and yield (Ahmed *et al*., 2006b; Pettit, 2008; Palanivell *et al.*, 2013 a, b).

Utilization of humic substances, chicken litter biochar, and clinoptilolite zeolite in acidic soils as an example, can reduce Al^{3+} and Fe^{2+} thereby increasing soil available P (Borggaard *et al*., 2005). Moreover, P fixation in acid soils also can be reduced by increasing soil pH as availability of P increases with increasing soil pH. For example, most of P is available for plant uptake at neutral pH (Havlin *et al*., 1999). Because of the basic nature of crude humic substances, chicken litter biochar, and clinoptilolite zeolite, these amendments can be exploited to increase pH of acidic soils.

The high CEC of rice straw compost, chicken litter biochar, and clinoptilolite zeolite can be exploited to improve CEC of acid soils so as enable these soils to temporary retain nutrients. This is possible because amending nitrogenous, phosphatic, and potassic fertilizers with crude humic substances, chicken litter biochar, and clinoptilolite zeolite will create a pool of negative charges around nutrients to retain and release nutrients timely for plant use (Brady and Weil, 2008). Temporary retention nutrients of nitrogenous, phosphatic, and potassic fertilizers at exchange sites can also mitigate nutrient leaching problem in acidic soils.

Ammonia volatilization from urea can be reduced with application of materials which are high in CEC (Latifah *et al*., 2011; Omar *et al*., 2010; Sommer *et al*., 2006). Humic substances, chicken litter biochar, and clinoptilolite zeolite, which are high in CEC, have been used to control ammonia volatilization in non-waterlogged condition (Zhao *et al*., 2013; Taghizadeh-Toosi *et al*., 2011; Spokas *et al*., 2011). For an example, proper retention of ammonium ions during hydrolysis of urea can reduce N loss through ammonia volatilization. Thus, this approach can improve nutrient recovery efficiency in manner that could translate into sustainable increase in rice yield. Besides reducing cost of fertilizers, the approach will also contribute to reduction of environmental pollution. Therefore, there is a need to amend nitrogenous, phosphatic, and potassic fertilizers with crude humic substances, chicken litter biochar, and clinoptilolite zeolite to improve soil chemical properties of the acid soils used for lowland rice cultivation in Malaysia besides increasing rice yield.

An overview of this study is presented in Figure 1.1. Chapter 4 focuses on the possibilities of minimizing ammonia loss from nitrogen fertilizers using organic and mineral amendments. Chapters 5 and 6 cover laboratory assessment on nutrients availability, retention, releases, and pH buffering capacity following the use of organic and mineral amendments. Selection of potential germination medium to produce better seedlings for pot and field studies had been covered in Chapter 7. Chaper 7 also focuses on the selection of promising organic and mineral amendments rate from pot study to be further evaluated in field study. Chapters 8 and 9 discuss on the sustainability of organic and mineral amendments in relation to rice yield, growth, nutrients uptake, nutrients recovery efficiency, and agronomic efficiency (field trials). Chapter 10 emphasizes on the economic viability of adopting organic and mineral amendments in lowland rice cultivation on an acid soil (*Typic Paleudults*).

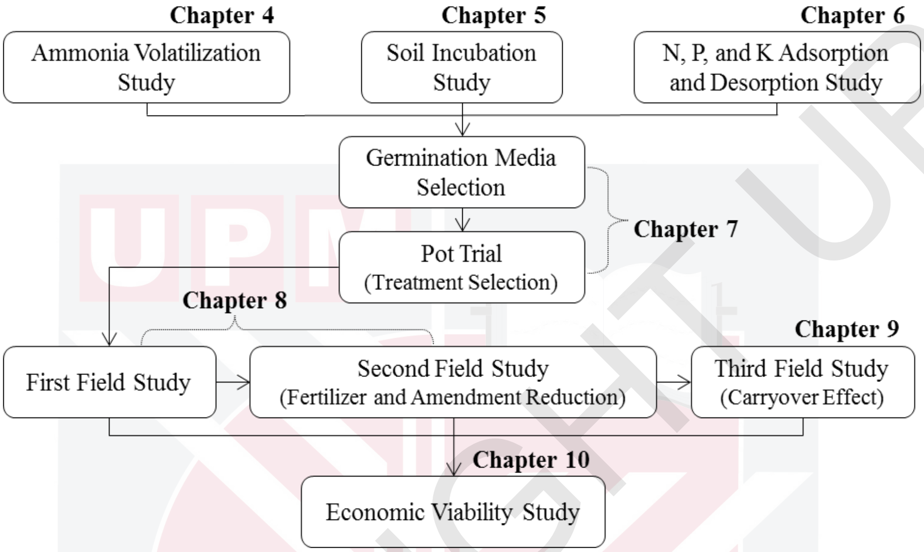

Figure 1.1: An overview of the study

The general objective of this study was to increase rice yield, nutrient recovery efficiency, and selected soil chemical properties. The specific objectives of this study were to determine the:

i. effects of mixing an acid soil (*Typic Paleudults*) with crude humic substances, chicken litter biochar, and clinoptilolite zeolite on ammonia volatilization from urea and selected soil chemical properties
ii. effects of an acid soil (*Typic Paleudults*) with crude humic substances, chicken litter biochar, and clinoptilolite zeolite on selected soil chemical properties over 120 days in a laboratory condition
iii. effects of amending *Typic Paleudults* with crude humic substances, chicken litter biochar, and clinoptilolite zeolite on adsorption, desorption of N, P, and K, and pH buffering capacity
iv. effects of mixing an acid soil (*Typic Paleudults*) with crude humic substances, chicken litter biochar, and clinoptilolite zeolite in waterlogged condition on rice plant growth, nutrients uptake and recovery, and selected soil chemical properties
v. effects of amending Bekenu Series (*Typic Paleudults*) with crude humic substances, chicken litter biochar, and clinoptilolite zeolite with the minimal application of conventional fertilizers on MR219 rice plant growth variables, yield, nutrients uptake, nutrients recovery efficiency, and selected soil chemical properties

vi. carryover effect (third planting cycle) of crude humic substances, chicken litter biochar, and clinoptilolite zeolite with minimal application of chemical fertilizers on MR219 rice plant growth, yield, nutrients uptake, nutrients recovery efficiency, and selected *Typic Paleudults* (Bekenu Series) chemical properties

vii. economic viability of including crude humic substances, chicken litter biochar, and clinoptilolite zeolite in rice cultivation compared with conventional practice (100% chemical fertilization).

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Gold Medal, *Increasing rice yield through biological agriculture*. 25th International Invention, Innovation & Technology Exhibition, ITEX 2014, Kuala Lumpur, Malaysia

Silver Medal, *Sustainable technology for increasing rice yield*. BioInnovation Awards 2013, Persada Johor International Convention Centre, Malaysia

Silver Medal, *Sustainable technology for increasing rice yield*. Malaysia Innovation Expo, MIExpo 2013, Universiti Putra Malaysia, Serdang, Malaysia

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