UNIVERSITI PUTRA MALAYSIA

SOIL NUTRIENTS AND MAIZE RESPONSES TO ELEMENTAL SULPHUR AS A FERTILIZER AND SOIL AMENDMENT FOR BINTANG SERIES SOIL

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By

MEHDI KARIMIZARCHI

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

February 2015

DEDICATION

THIS THESIS IS DEDICATED TO

MY PARENTS, WIFE AND CHILDREN

WITH INNERMOST AND EVERLASTING AFFECTION AND LOVE

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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February 2015

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High pH soils accounts for more that 30 percent of world soils. Although the distribution of these soils in Malaysia is not well documented, there are some high pH soils, found all over the country, which are affected by the limestone materials. Alkaline soils pose problems to plant nutrient availability especially micronutrients, in which for each unit increase in soil pH the activity of ferrous iron, Zn, Mn and Cu decreases about 100 times. Increasing the release of indigenous soil nutrients and supplying the plants with external sources of available nutrients are two well-known agronomic approaches for alleviation of these problems. Elemental sulphur as a cheap and readily available source of soil acidulate possess the slow release characteristics that is produced as a by-product of oil refinery may be a useful material for alleviating some alkaline soil problems. The objective of the present project was to evaluate the ability of high pH Malaysian soils to oxidize elemental sulphur and to evaluate selected soil and plant responses to soil acidification using elemental sulphur.

In the first study, Bintang Series soils located in Perlis was selected and analyzed for soil physicochemical properties. It was found that the soil was inherently infertile, characterized by low organic matter and nutrient content. Soil was found to be slightly alkaline in nature with the pH value of 7.5 which is affected by limestone materials. The soil was poor in available micronutrients, nitrogen, sulphur and phosphorus that could lead to their shortage for plants. In addition, the total N, S, Cu and Zn in the soil were very low and these nutrients should be applied for long term and sustainable agricultural practices. However the release of indigenous Fe, Mn and K, which were found in high amounts, can be employed to increase their available fraction. Therefore, it is most likely that successful agricultural practices needs addition of soil amendments or fertilizer application to prevent nutrient deficiency.

The second study evaluated the ability of Bintang Series soil in oxidation and incorporation of elemental sulphur. To quantify elemental sulphur oxidation and transformations in this soil, it was treated with 6 rates of elemental sulphur and sampled 8 times during 75 days of incubation in laboratory conditions. Results demonstrated that elemental S, applied up to 1 g S kg^{-1} soil, was successfully biologicaly oxidized and converted to both organic and inorganic forms. While sulphate, as inorganic water soluble S, appeared to be the predominant form in the soil treated with 0.25 g S kg^{-1} and more, organic forms of S were the major form when the soil was amended with 0.12 g S kg^{-1} and less. In the third study, the effect of elemental sulphur on urea transformations was elucidated. The results showed that ammonia volatilization was the major pathway and application of elemental sulphur can significantly decrease it from 80 percent at untreated soil to only 30 percent in Bintang Series soil treated with 2 g S kg^{-1} soil. In the fourth study, after 0, 20 and 40 days of soil incubation with different amounts of elemental sulphur including 0, 0.5, 1 and 2 g S kg^{-1} of soil, maize plants were grown for 45 days under glasshouse conditions. Plants received 0.5 and 1 g S kg^{-1} soil showed maximum performance with 45 percent increase in total dry weight. Results of plant analysis revealed that this is due to the increase in S, Zn and Mn content of maize leaves, stem and root from deficient in un-amended to sufficient level in amended plants. Additionally, excessive sulphur addition resulted in Zn and Mn toxicity with 57.5 percent reduction in maize biomass. The results of soil analysis showed that addition of elemental sulphur decreased soil pH and consequently the concentrations of soil nutrients increased. While this resulted in higher concentration of some nutrients, such as S, Mn and Zn, in maize, the Cu, P and Ca content of treated plants were decreased. The results of fifth study that was aimed to elucidate the effect of elemental sulphur on the nutrient release and its relationship with soil pH exhibited that addition of elemental sulphur significantly increased concentration of all nutrients in Bintang Series soil. Additionally, the release and mobility of each nutrients started at specific pH. While that of Ca and Mg started with small increase in acidity, the pH value at which Cu, Fe, Al, Zn and Mn concentration significantly increased are 3.94, 3.94, 5.26, 5.26 and 6.29 respectively. In conclusion, result of studies confirmed the ability of Bintang Series soils in biological oxidation of elemental sulphur. The results also showed that addition of elemental sulphur increased soil nutrient concentration, alleviated S, Mn and Zn deficiency and reduced Ca, P and Cu concentrations in maize. When used in appropriate amounts, 0.5 g S kg^{-1} soil or 750 kg S ha^{-1}, elemental sulphur can efficiently enhance soil fertility and maize performance by providing macro and micro nutrients for balanced fertilization.

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

KESAN ELEMEN SULFUR KE ATAS TANAH DAN JAGUNG SEBAGAI BAJA DAN PERAPI TANAH PADA SIRI TANAH BINTANG

Oleh

MEHDI KARIMIZARCHI

Februari 2015

Pengerusi: Professor Madaya Aminuddin Hussin, PhD
Fakulti: Pertanian

Terdapat tiga puluh peratus tanah di dunia mempunyai kandungan pH yang tinggi. Walaupun taburan tanah yang mempunyai kandungan pH yang tinngi di Malaysia tidak didokumentasikan, namun terdapat tanah sedemikian di serata negara akibat daripada proses luluhawa di kawasan yang mempunyai kapur. Tanah beralkali menyumbang masalah kepada kesedian nutrisi tumbuhan terutamanya mikronutrisi, di mana kenaikan pH menyebabkan unsur seperti Besi (Fe), Zink (Zn), Mangan (Mn) dan Tembaga (Cu) berkurangan sebanyak 100 kali. Dua kaedah agronomi yang biasa dicadang untuk menyelesaikan masalah ini, iaitu dengan menambah bahah yang mempunyai nsur-unsur berkenaan ke dalam tanah, dan juga membekalkan unsur-unsur secara terus kepada tumbuhan melalui baja mikronutrisi. Elemen Sulfur (S) yang murah dan mudah diperolehi boleh dijadikan sebagai sumber untuk menurunkan keasidan tanah. Elemen ini juga mempunyai sifat untuk membebaskan unsur sulfur ke dalam tanah secara perlahan mengikut masa. Elemen S terjadi daripada hasil penyulingan minyak mungkin pilihan yang sesuai untuk menyelesaikan masalah tanah beralkali. Antara objektif-objektif dalam projek ini adalah untuk menilai kebolehan tanah di Malaysia mengoksidakan elemen S, dan mengkaji tindak balas tanah dan tumbuhan terhadap keasidan tanah menggunakan elemen S. Di dalam kajian yang pertama, tanah Siri Bintang yang diperolehi dari Perlis telah dipilih dan dianalisa untuk ciri-ciri fizik-kimia tanah. Kajian mendapati tanah tersebut tidak subur disebabkan oleh kandungan organik dan nutrisi yang rendah. Tanah tersebut juga didapati sedikit beralkali dengan nilai pH 7.5 akibat daripada campuran bahan batu kapur. Andaian awal kami terhadap pH tanah yang tinggi disokong apabila tanah tersebut tidak subur dari segi kekurangan kesediaan unsur-unsur mikronutrisi, Nitrogen (N), Sulfur (S) dan Fosforus (P) untuk kegunaan tumbuhan. Walau bagaimanapun, jumlah unsur-unsur seperti Fe, Mn dan Kalium (K) yang dijumpai di dalam adalah tinggi. Oleh.itu, untuk mewujudkan amalan pertanian yang berjaya, kita perlu menambahkan baja atau bahan-bahan lain untuk

mengelakkan daripada kekurangan nutrisi pada tanaman. Kajian kedua adalah untuk menilai kebolehan tanah Siri Bintang dalam pengoksidaan dan gabungan elemen S. Bagi mengukur pengoksidaan elemen S dan transformasi di dalam tanah ini, tanah dirawat dengan 6 kadar elemen S dan sampel di ambil sebanyak 8 kali selama 75 hari secara inkubasi di dalam makmal. Keputusan menunjukkan elemen S yang diberi sebanyak 1 g S kg^{-1} tanah telah berjaya dioksidakan dan ditukar kepada bentuk organik dan bukan organik. Manakala sulfat sebagai bahan bukan organik yang larut di dalam air, menjadi dominasi di dalam tanah yang dirawat dengan 0.25 g S kg^{-1}, dan S di dalam bentuk organik menjadi bentuk yang utama apabila tanah dirapikan dengan 0.125 g S kg^{-1} dan ke bawah. Dalam kajian yang ketiga, selepas tanah diinkubasi pada hari 0, 20 dan 40 dengan jumlah elemen S yang berbeza termasuk 0, 0.5, 1 dan 2 g S kg^{-1} tanah, pokok jagung ditanam selama 45 hari di dalam persekitaran rumah kaca. Pokok yang menerima 0.5 dan 1 g S kg^{-1} tanah menunjukkan prestasi yang maksimum dengan peningkatan sebanyak 45% di dalam jumlah berat kering. Keputusan analisis pokok ini menunjukkan peningkatan kandungan S, Zn dan Mn di dalam daun jagung, batang dan akar daripada tahap tidak mencukupi pada pokok yang tidak dirapi menjadi tahap mencukupi pada pokok yang dirapi. Tambahan lagi, penambahan sulfur yang berlebihan menunjukkan kesan toksik pada unsur Zn dan Mn dengan penurunan sebanyak 57.5 peratus pada biojisim jagung. Keputusan analisis tanah juga menunjukkan penambahan elemen S telah menurunkan pH tanah dan pada masa yang sama telah meningkatkan kepekatan nutrisi tanah. Apabila kepekatan sesetengah nutrisi seperti S, Mn dan Zn di dalam pokok jagung meningkat, kandungan elemen lain seperti Cu, P dan Ca pula berkurangan pada pokok yang dirawat. Keputusan bagi kajian yang keempat yang bertujuan untuk mengukur elemen S pada nutrisi yang dibebaskan dan hubungan mereka dengan pH tanah, telah menunjukkan penambahan elemen S berjaya juga meningkatkan kepekatan semua nutrisi di dalam tanah Siri Bintang. Tambahan lagi, pembebasan dan pergerakan untuk setiap nutrisi bermula pada pH yang spesifik. Manakala unsur Ca dan Mg pula bermula dengan peningkatan yang sedikit pada keadaan berasid, dan kepekatan unsur Cu, Fe, Al, Zn dan Mn meningkat secara ketara pada pH 3.94, 3.94, 5.26, 5.26 dan 6.29 masing-masing. Kesimpulannya, hasil daripada kajian menunjukkan tanah Siri Bintang berkebolehan dalam pengoksidaan elemen S. Keputusan juga menunjukkan penambahan elemen S turut meningkatkan kepekatan nutrisi, mengatasi masalah kekurangan unsur S, Mn dan Zn dalam tanah serta meningkatkan unsur Ca, P, dan Cu di dalam jagung. Dengan pemberian jumlah elemen S yang sesuai, 0.5 g S kg^{-1} tanah or 750 kg S ha^{-1}, ia boleh meningkatkan kesuburan tanah dan tumbesaran pokok jagung secara berkesan melalui keseimbangan unsur-unsur makro dan mikro nutrisi.

ACKNOWLEDGEMENTS

First and foremost, my honest appreciation to my supervisory committee, who were involved in my training towards obtaining this degree. I am most grateful to Associate Professor Dr. Aminuddin Hussin, chairman of my supervisory committee for her patience, tireless support, willingness to help, encouragement, kindness and guidance throughout the research and during the preparation of the thesis. I am very much indebted to the members of my supervisory committee, namely Professor Dr. Mohd Khanif Yusop and Associate Professor Dr. Radziah Othman for their suggestions and guidance towards the completion of this study. I would also like to extend my thanks to late Associate Professor Dr. Anuar Abd. Rahim for his valuable discussions in statistical analysis. I would like to extend my deep and sincere appreciation to Universiti Putra Malaysia and all staff members of the Department of Land Management who enabled me to continue my study in UPM. They have changed my life to the right way.

I am very thankful to all of my friends for their help, cooperation and friendship: Ahmad Shakerardakani, Mohammadreza Naroueerad, Babak Khayyambashi, Hamed Zakikhani, Amin Soltanqaisi, Nafisah Alifar, Golnaz Sharifiipur, Shahram Mahmoodsoltani, Mohammadtaqi Karbalaee, Rizal Mohd Arifin and Kang Seong Hun. Finally, this project would not be possible without support from my family members. My heartfelt thanks and appreciation goes to my friends Alireza Majidi, Sadeq Ashkani, Mohammadreza Khammar, Saeed Rahmanian, Seyyedmoosa Sadeqi, Hamidreza Naji, Abbas Abdollahi, Farzanah Ahmadi, Sistani, Mohammadreza Eshqi, Majid Abdorrazaq for their love and encouragement.

APROVAL

I certify that an Examination Committee has met on 22-1-2015 to conduct the final examination of Mr. Mehdi Karimizarchi for his Doctor of Philosophy thesis entitled "SOIL AND MAIZE RESPONSES TO ELEMENTAL SULPHUR AS A SOIL AMENDMENT FOR BINTANG SERIES SOIL" in accordance with Universities and University Colleges 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

Members of the Thesis Examination Committee were as follows:

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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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LIST OF ABBREVIATIONS

ºC	Degree centigrade
CEC	Cation exchange capacity
CMRs	Chlorophyll meter readings
CRD	Completely Randomized Design
DMRT	Duncan multiple range test
EC	Electrical conductivity
g	gram
g kg^{-1}	gram per kilogram
HPLC	High performance ion chromatography
IC	Ion chromatography
ICP-AES	Inductively coupled plasma - atomic emission spectrometry
IWSS	Inorganic water soluble sulphur
LAI	Leaf area index
mg	milligram
ml	milliliter
mm	millimeter
MS	Mean square
OWSS	Organic water soluble sulphur
ppm	Part per million
RCBD	Randomized Complete Block Design
SAS	Statistical Analysis Software
TWSS	Total water soluble sulphur
Tr	Traces
µg	microgram

CHAPTER 1

INTRODUCTION

High pH soils pose problems to plant nutrient availability especially micronutrients, for each unit increase in soil pH the activity of ferrous iron, (plant available form), zinc, Mn and Cu decreases about 100 times (Lindsay, 1979; Marschner et al., 2012; Sanaeiostovar et al., 2011). In addition, low nitrogen efficiency is experienced due to high ammonia volatilization (Liu et al., 2007). For instance, Pacholski et al. (2006) reported that around 48 percent of applied urea (200 kg ha^{-1}) was volatilized as NH_3 under conditions of field study in China. The likelihood of ammonia volatilization up to 80 percent of added urea under field conditions was released by Gould et al. (1986). It should be noted that urea accounts around 70% of total nitrogen fertilizers (Glibert et al., 2006).

High pH soils accounts for more that 30 percent of world soils (Manahan, 2004; Shenker et al., 2005). These soils that are mainly located in arid regions amount to about 50 million squar kilometres. There are additional areas that have soils that are alkaline, such as the regions where loessial materials (wind-blown soil dust sourced from more arid regions) containing calcium carbonate have been deposited, or where soils have developed on calcareous parent materials. Alkaline soils, soils with the pH of more than 7, can be found in isolated several areas in Malaysia especially in areas nearby to limestone hills and such hills occur widely in Malaysia (Tan, 2002). In Peninsular Malaysia, the major areas are located in the Klang Valley, the Kinta Valley, the Kedah-Perlis region (including the Langkawi Islands), Kelantan (Gua Musang area), and Pahang.

The Bintang Series soil is located in Perlis at the northern part of the west coast of Peninsular Malaysia and has the Satun and Songkhla Provinces of Thailand on its northern border. Perlis is bordered by the state of Kedah to the south. It was known that the soil located in Pusat Pertanian Bkuit Bintang, Perlis is formed by limestone parent materials and its pH varies from 7.3 to 8 (Noor, 2006). It is also low in organic matter and nitrogen. As a result, it is expected that soil nutrient availability to crops is low and necessitated proper fertilizer management practices. In line with our expectations, Mohd. Razi (1996) reported the incidence of insidious fruit rot for mango grown in alkaline soil of Bukit Bintang with the pH range of 7.23 to 8.4, located in Perlis. He also found that application of Biomin Ca fertilizer reduced the incidence of insidious fruit rot in mango and increased the marketable fruits. Additionally, as the Bintang Series soil is high in pH the expectation is that the applied urea would loss through ammonia loss `(Aminuddin, 1994; Haruna Ahmed et al., 2008). However, little is known about the chemical characteristics of Bintang Series soil and the ammonia volatilization potential. It should be noted that Department of Agriculture (DOA) of Malaysia has recently opened the new lands for agricultural activities in Perlis, as the smallest state in Malaysia. Therefore, there is a need to provide the dearth of information.

Increasing the availability of indigenous soil nutrients, supplying the plants with external sources of available nutrients and increasing plant efficiency in nutrient uptake and translocation are the three main agronomic approaches to the alleviation of nutrient deprivation in high pH soils (Shenker & Chen, 2005). The agronomic practices may include foliar application of micronutrient, soil fertilization using inorganic fertilizers, industrial by-products, synthetic chelates and organic complexes, soil management and rhizosphere manipulation to increase the availability of indigenous soil nutrient.

In general, soil acidification is known as an effective strategy to enhance the solubility of indigenous soil nutrients (Viani et al., 2014) and its key importance was stated by Brady et al. (2002) ‘‘No other single chemical soil characteristic is more important in determining the chemical environment of higher plants and soil microbes than the pH.’’ As different soils have various responses to acidification treatment and a different optimum pH may exist, this pH should be identified to avoid unnecessarily extreme acidification of soils. The extreme soil acidification may results in toxicity of those elements in plants and it appears to be partly due to a nutrient imbalance brought about by abnormal accumulation in plant tissue.

There are several options to acidify high pH soils including elemental sulphur, sulfuric acid, iron sulfate, aluminum sulfate, ammonium fertilizers, especially ammonium sulfate, and sphagnum peat (Chein, 2011). However elemental sulfur, possessing slow-release characteristics, has attracted the attention of researchers most because; firstly, one ton of sulfur is equivalent to three tons of sulfuric acid and 6.9 tons of aluminum sulfate. Secondly, its transport does not need special considerations. Thirdly, as a by-product of oil refinery, it is readily available and cheap. Besides, elemental sulfur is pure and its effects on soil and plant properties is free of interferences.

The diverse effects of elemental sulphur on soil chemical properties and plant growth was reported (Perucci et al., 2010; Sameni et al., 2004; Schmidt et al., 2012; Skwierawska et al., 2012). For instance while significant increase in available K, P and Zn in soil due to application of elemental sulphur up to 448 kg ha^{-1} was reported by Ye et al. (2011) Sameni and Kasraian (2004) showed that soil nutrient release was not affected by application of elemental sulphur up to 6 t ha^{-1}. However the contribution of elemental sulphur in high pH soils of Malaysia has not been documented. Additionally, when elemental sulphur was added to the agricultural soils it will undergoes several different path ways such as oxidation, mineralization, immobilization, adsorption and leaching (Scherer, 2009). It also may convert to different forms such as inorganic water soluble, organic water soluble and adsorbed sulphur (Shan et al., 1997; Ye et al., 2010). As the extent of these transformations depends on the soil chemical properties and sulphur management, it is essential that the incorporation of elemental sulphur be studied for each specific soil.

1.1 Hypothesis

We hypothesized that with application of elemental sulphur to the Bintang Series soil it would be converted to the protons and sulphate. It also assumed that the protons would decrease soil pH and increase available soil nutrients. Our expectation was that with increasing the availability of soil nutrients the plant nutrient content and performance would be affected. In addition we hypothesized that addition of elemental sulplhur would decrease nitrogen loss through ammonia volatilization.

1.2 Objectives

The overall objective of the work presented here was to obtain the knowledge required to optimize plant availability of nutrients in appropriate quantities and in synchrony with plant demand. They were:

1. To characterize the physico- chemical properties of Bintang Series soil and to evaluate its inherent fertility situation.
2. To quantify sulphur forms and its transformations in Bintang series soil amended with elemental sulphur.
3. To investigate the role of elemental sulphur on the urea transformations and ammonia loss.
4. To elucidate the effect of elemental sulphur on release of soil nutrient and its relationship with soil pH.
5. To evaluate the remediation effect of elemental sulphur on growth of maize.

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