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Formulation of Coal Fly Ash and Sewage Sludge Mixtures to Reduce Impacts on the Environment When Used as Soil Ameliorant for Acidic Tropical Soils

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ABSTRACT

Use of coal fly ash (CFA) as a soil ameliorant is hindered by the lack of macronutrients in the ash, besides, there are also concerns about its high concentration of microelements, especially boron. Sewage sludge (SS) on the other hand, has a high amount of macronutrients especially nitrogen. However, it also contains high concentrations of micronutrients especially Zn. This study was carried out to evaluate the potential of CFA as a soil ameliorant to immobilize heavy metals from SS-treated soil and whether the SS could provide supplementary macronutrients for maize growth requirement. A laboratory soil incubation study was conducted using 3 kg mixture of soil, SS and CFA. In all treatments, the SS was applied at 5% w/w. The rates of coal fly ash varied from 0, 2.5, 5, 10, 20 and 40% w/w. The soil solution was collected and analyzed weekly for pH and soluble Zn, Cu and B. A similar experiment was conducted in a glasshouse but using CFA at rates up to only 20% w/w on maize as a test plant. Although the acid neutralizing capacity of this CFA is only 0.50% of calcium carbonate equivalent (CCE), the high rates of CFA application increased the soil solution pH. Treatments of CFA at 10% and above reduced Zn concentrations in soil solution to less than 1 mg L^{-1}. The reduction in Cu and B concentrations in the soil solution were not apparent in this study. Uptake of Zn by the maize plants was found to significantly decreased in treatments of 10% CFA and above. Nitrogen uptake by maize decreased in the treatment using more than 10% CFA. Only the highest treatment of CFA (20% w/w) exceeded the B toxicity level for maize (98-100 mg kg^{-1}). Coal fly ash and sewage sludge mixture can be used as a soil ameliorant provided attention is given to the B toxicity and P and K deficiency problems that might be faced by plants such as maize.

Keywords: acidic tropical soil, glasshouse study, maize plants, soil solution study

INTRODUCTION

Man has applied non-hazardous industrial wastes on land such as sewage sludge (SS) and coal fly ash (CFA) for centuries as a mean of disposal as well as to improve the soil via recycling of nutrients and addition of organic matter. Due to economic constraints and environmental concerns of 1andfilling and incineration methods, interest in land application of industrial wastes has continued to grow.

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Recycling of these wastes to agricultural land can supply the soil with essential plant nutrients and organic matter. However, the applications of these wastes to soil may also have adverse effects due to the presence of heavy metal concentrations which will affect soil health, food quality as well as the environment. Therefore, this move to recycle these waste on land is of great public concern.

One of the reasons for the poor acceptance of waste materials such as CFA and SS as soil ameliorant is because it may cause plant nutrient imbalance, either due to deficiencies or excesses of one or several elements. Coal fly ash is an amorphous aluminosilicate material, a by-product of coal combustion and is composed of particulate matter collected from flue gas stream. Coal is one of the alternative natural resources used for the production of electricity in Malaysia. The increasing use of coal for electric power generation will generate large quantities of CFA. Kapar power station in Selangor, Malaysia, produces around 200 Mg CFA per day. The increasing amount of CFA has given rise to serious disposal problems. Currently, only 20% of the CFA is utilized as a component in cement mixture, the rest being left stacked within the vicinity of the power plant. Coal is known to contain every naturally occurring element, and therefore, it is not surprising that CFA can have significant beneficial effect on solving certain problems of soil quality. For example, the high pH and low S coal fly ash has found application as a liming agent (Adriano *et al*. 2002). Also, the CFA is rich in trace elements and has been successfully applied to alleviate micronutrients deficiencies (Adriano 2001).

Another potentially beneficial industrial by-product is the SS. Malaysia produces about 5 million m3 of SS per year and by the year 2020, the amount is expected to increase to 6.6 million m3 (Indah Water Konsortium Sdn. Bhd. 1997). Hence, commercializing SS as a soil ameliorant should offer great economic potential in the future. The application of SS to agricultural land is generally the most economical means of waste disposal and also provides an opportunity to recycle beneficial plant nutrients and organic matter to soil for crop production. The value of SS as N and P fertilizer replacement for example, has been frequently reported (Kelling *et al.* 1977; Rosazlin *et al*. 2005). Sewage sludge can also supply other plant nutrients such as Mg, Ca, Zn and Cu, but their importance will depend on whether these nutrients are deficient in the soil. Organic matter in SS can increase crop productivity by improving soil physical and chemical properties (Adriano *et al*. 2002). However, long-term application of sludge can lead to significant accumulation of heavy metals especially Cu and Zn in soil and plants and can cause heavy metal toxicity (McGrath *et al.* 1995). High heavy metals concentrations in soils can pose detrimental effects such as metal toxicity to plants.

In many cases, a single byproduct may not be ideal by separate from itself for land application, but through co-utilization of byproducts, more useful agronomic products may result. The benefits of co-utiliszation may include better nutrient balance, reduction in toxins or contaminants, improved moisture content, improved economic value, improved soil conditioning effects, etc. Therefore, the objectives

of this study were to evaluate whether CFA can be utilized as soil ameliorant to immobilize heavy metals from SS-treated soil and whether the SS could provide adequate macronutrients for plant growth requirement.

MATERIALS AND METHODS

Coal fly ash was collected from Sultan Salahuddin Abdul Aziz power station in Kapar, Selangor, Malaysia and the SS was collected from Indah Water wastewater treatment plant in Gombak, Selangor, Malaysia. The soil used throughout this study was the topsoil (0-20 cm) of a Bungor Series soil (clayey, kaolinitic, isohyperthermic family of a Typic Paleudult) (Tessens and Shamshuddin 1979). The CFA, SS and soil samples were air-dried, ground, and sieved through a 2.0 mm sieve before the laboratory analyses were conducted.

Chemical Properties of CFA, SS and Soil

The chemical properties of the CFA, SS and soil analyzed are listed in Table 1. The pH was determined using 1:2.5 soil:water (w/v) using Beckman Digital pH meter. The EC was measured from a solution collected from the saturated paste using the Radiometer EC meter. Soil exchangeable bases (K^+, Ca^{2+} and Mg^{2+}) and cation-exchange capacity (CEC) was determined by 1N NH_4OAc, buffered at pH 7.0 leaching method (Thomas 1982). The leached basic cations were then determined by the Perkin Elmer PE 5100 atomic absorption spectrophotometer (AAS). The adsorbed NH_4^+ was then displaced with K_2SO_4 solution and determined using Quickchem, FIA 8000 auto-analyzer (Lachat Instruments, Milwaukee, WI, USA).

Total carbon was determined by a combustion technique using a CR-412 carbon analyser (LECO Corporations, St. Joseph, USA). Total nitrogen was determined using the modified Kjeldahl method (Bremner and Mulvaney, 1982). Total heavy metals were extracted using the aqua-regia solution (1:3 HNO_3:HCl), after which the metals were determined using Perkin Elmer PE 5100 AAS. Boron was extracted with hot water and extracts determined by the colorimetric azomethine method (Bingham 1996). The acid neutralizing capacity (ANC) was determined by a batch titration method using an incremental volume (0, 5, 10, 15, 20 and 25 mL) of 0.5 M HCl to 10 g of the samples and the final volume was made up to 25 mL with deionized water. These samples were left to equilibrate for 1 week after which the pH values were read. The same procedure was conducted with calcium carbonate. The ANC, which was expressed as calcium carbonate equivalence (CCE), was calculated based on the amount of acid required to obtain a pH of 7.0 in comparison with the amount obtained when calcium carbonate was used.

Soil Incubation Study

A laboratory incubation study was carried out at room temperature (28o C), whereby CFA at either 0, 2.5, 5, 10, 20 or 40% (w/w) was added to a Bungor Series soil treated with 5% SS (w/w). The rate of 5% SS was established in earlier

studies (Rosazlin *et al.* 2005, 2006). A 3-kg total weight of soil mixture (soil + SS + CFA) was placed in a pot. Twenty-four pots were arranged in a completely randomized design (CRD), which consisted of six treatments and four replicates.

TABLE 1
Chemical properties of coal fly ash, sewage sludge and Bungor series soil used in this study

	CFA	Sewage sludge	Bungor Series Soil
pH	8.34	4.42	4.72
E.C. (dS m^{-1})	1.31	n.d.	n.d.
CEC (cmol (+) kg^{-1})	0.04	n.d.	6.07
ANC %	0.50	n.d.	n.d.
Total C %	5.32	31.02	0.97
Total N %	0.32	3.33	0.06
Total P %	0.15	0.48	n.d.
Extract. P (mg kg^{-1})	n.d.	n.d.	3.12
Exch. K %	0.34	3.75	0.31
Exch. Ca %	0.97	0.21	0.52
Exch. Mg %	0.44	0.87	0.17
Total Zn (mg kg^{-1})	82.27	2300	n.d.
Total Cu (mg kg^{-1})	43.73	107	n.d.
Extract. Zn (mg kg^{-1})	n.d.	n.d.	1.80
Extract Cu (mg kg^{-1})	n.d.	n.d.	0.40
Extract B (mg kg^{-1})	727.50	n.d.	n.d.

n.d. - not determined

The in-situ soil solutions from the incubation study were sampled using a rhizon soil moisture sampler (Eijkelkamp, the Netherlands). This consisted of a length of porous, chemically inert hydrophilic plastic (2.5 mm o.d., 1.4 mm i.d., average pore diameter ca. 0.1 µm), capped with nylon at one end, and a connector for attaching a vacuum syringe (10 mL) to extract the soil solution. Deionized water was added to the soil at 21% of moisture content (field capacity is 16%). The porous tip of the rhizon soil moisture sampler was pushed into the soils. After 48 hours, about 10 mL of the soil solutions were collected from each of the syringes. The soil was incubated in the laboratory for 70 days and the soil solutions were collected at a weekly interval. The soil solution from each treatment was analyzed for pH, water soluble B, Cu and Zn.

Glasshouse Study

The study was conducted in a glasshouse unit of the Faculty of Agriculture, Universiti Putra Malaysia, Malaysia. Twenty pots were arranged in a completely randomized design (CRD). There were five treatments with each treatment being replicated four times. The treatments were similar to the treatments used in the soil incubation study; except for CFA at a rate of 40% w/w was removed because the rate was too

high for practical application. Maize (*Zea mays* L.) was used as the test crop and three plants per pot were grown in 3-kg soil mixture (soil + SS (5% w/w) + CFA). To each pot, P was applied at 100 kg P ha^{-1}as triple superphosphate (TSP) and K was applied at 140 kg of K ha^{-1} as muriate of potash (MOP) for all treatments.

Soil Chemical Analyses

The dried CFA-amended soil samples were analyzed for pH (1:2.5 soil:H_2O ratio), and electrical conductivity (EC) (1:5 soil:H_2O).

Plant sample preparation and analyses

Maize was harvested at maturity, 70 days after planting. After harvest, fresh and dry plant weights were determined. Then the maize tissue was dried in an oven (65-70^oC) until a constant weight was recorded. The dried tissue was ground to pass a 0.1 mm sieve. Macronutrients (P, K, Ca and Mg) and micronutrients (Cu and Zn) in the tissue were extracted out using the dry ashing method. Between 1 and 2 g of oven-dried tissue sample were ashed in a muffle furnace at 300^oC for one hour, and at 500^oC for a further four hours. The cool ash was digested again with a few drops of deionized water and 2 mL of concentrated HCl, and then heated again on a hot plate for 15 minutes. Then 10 mL of 20% nitric acid was added and the digest was further heated in a water bath at 100^oC for one hour. It was then filtered into a 100 mL volumetric flask and made up to volume with distilled water. The macronutrients (K, Ca and Mg) and micronutrients (Zn and Cu) in the plant digest were determined using the Perkin-Elmer PE 5100 AAS. Phosphorus was determined using Quickchem, FIA 8000 auto-analyzer (Lachat Instruments, Milwaukee, WI, USA). Nitrogen was determined using Kjeldahl digestion method while B was determined by the azomethine method after extraction with hot water. Uptake of macro- and micronutrients by maize plants were calculated by multiplying the concentrations of these elements in the plant tissue with the dry weight of the plant.

The validity of the dry ashing procedure and the AAS operating parameters was established using the National Institute of Standard and Technology (NIST) maize grain standard reference material, NIST 8433. The data obtained were subjected to analysis of variance (ANOVA) using the Statistical Analysis System (SAS Institute Inc. 2004) and, where significant, the means were compared by using Duncan Multiple Range Test (DMRT).

RESULTS AND DISCUSSION

Chemical Properties of CFA

The chemical properties of the CFA, SS and Bungor Series soil are shown in Table 1. The CFA is an alkaline residue produced during the burning of coal for the generation of electricity which is enriched with CaO and MgO and has a pH around 8 to 12. The pH of CFA can vary depending on the S contents of the coal source, with high S generally producing acidic material and low S producing alkaline

material (Adriano *et al.* 2002). The pH of CFA used for this study was 8.34. In some cases, an alkaline agent was used as a stabilization agent for SS to reduce pathogen and heavy metals availability (McGrath *et al.* 1995; Zhang *et al*. 2007). The CEC value for CFA has been not widely discussed in previous studies. Cation exchange capacity is usually used in soil characterization for soil classification as well as in assessing their fertility status. Since CFA is not considered a soil, this maybe one of the reason why CEC of CFA has not been widely discussed. From this study, the CEC value was found to be very low, 0.04 cmol(+) kg^{-1}. This indicates that this form of heavy metal complexes in CFA amended soil would not be influenced by the CEC. Coal fly ash has been reported to have very low CEC that varies from 0.5 – 1.0 cmol (+) kg^{-1} (Bilski *et al*. 1995).

The ANC is usually expressed as $CaCO_3$ equivalent and one of the most important factors used to evaluate the value of industrial byproducts for use as a liming agent on acidic soil. The neutralization of acid by CFA is a relatively slow process that mainly involves the particle surfaces (Wong *et al*. 2002). The CFA used in this study was not a good liming agent, with only 0.504% $CaCO_3$ equivalent (CCE). Based on the low level of Ca in this CFA (Table 1), it is considered only as a Class F fly ash (Bilski *et al*.,1995). Therefore, considerably large quantities of this CFA compared to lime will be required to raise the pH of soil to some target level.

The total C content of the CFA was 5.32% (Table 1). Since the C was likely to be oxidized into gaseous constituents during the combustion, it is usually present in negligible quantities (Bern 1976; Bilski *et al.* 1995). Nevertheless, C had been reported to be as high as 30% by weight in some CFA (Bern 1976).

The CFA alone is a poor source of N (Sajwan et al. 2003). Nitrogen is also volatilized during the process of coal combustion which drastically reduces the N quantity in the CFA. The N value for this CFA was 0.32% (Table 1) which is considered low for plant growth. A low value of N (0.20%) in CFA has also been reported in an earlier study (Jala and Goyal 2004).

Coal fly ash is a poor source of P as it has been found to be inferior to monocalcium phosphate (Martens 1971). The P level of the CFA in this study was 0.15% (Table 1), within the range reported by a previous finding (Page *et al*. 1977). Phosphorous concentrations in plant foliage have often been reduced by CFA applications (Elseewi *et al*. 1978; Molliner and Street 1982) which can be attributed to an increase in soil pH by the CFA and the formation on insoluble complexes (Adriano *et al*. 2002).

Available Ca, Mg and K content in this CFA was 1.27%, 0.29% and 0.18%, respectively. These results were within the range of a previously reported study on CFA; these were 0.11 – 22.2%, 0.04 – 7.6% and 0.15 – 3.5%, for Ca, Mg and K, respectively (Page *et al.* 1977).

All the heavy metals listed in Table 1 fall within the ranges found in most soils and allowable level of the European Communities Standards (ECS) for land application of waste. However, the microelement B was found to be very high.

Amending SS with CFA has been reported to reduce the availability of heavy metals in SS amended soils (Su and Wong 2003).

Boron Concentration

Coal fly ash generally has high B concentration and thus their application to agricultural soils should be critically evaluated in view of plant growth problems associated with B toxicity. According to numerous researchers, the only limitation in using CFA as a soil amendment is its high soluble B concentrations. Since B compound in soils is water soluble, the weathering of CFA by allowing adequate drainage should reduce the detrimental effect of B on plants (Elseewi et al. 1978; McGrath *et al.* 1995). Based on previous studies, a simple experiment was conducted with 10 g CFA being leached in a leaching tube with 1 L of deionized water. This study showed that B concentration in leached CFA was much lower (352.5 mg kg^{-1}) compared to the unleached CFA (727.50 mg kg^{-1}), proving that B in the CFA was highly leachable by water.

Soil Incubation Study

Soil solution is considered as the aqueous liquid phase of soil at field moisture content which represents the medium where soil chemical reactions take place (Molliner and Street 1982). Availability of elements, be it macro- or trace elements is mostly a function of solubility, therefore, a reliable technique to assess the availability of these elements for plant uptake or leaching is by extracting a solution from the soil (Zhang *et al.* 2007).

pH Effect

The pH values of the SS-treated soil incubated with different rates of CFA are presented in *Fig.1*. The pH values for all treatments increased with incubation time, and the increase in pH was greater with higher rates of CFA. In the first week of incubation, soil solution pH for treatments using 40% CFA was the highest (6.28) compared to other treatments and increased to 7.81 at week ten. In this pH range, the solubility of trace elements would be low, as adsorption and precipitation reactions would decrease their solubilities (Sajwan *et al*. 2003). However, complexation with soluble organic matter from SS may maintain trace elements' cationic species in solution (Brown *et al.* 2005). The pH for CFA used in this research was 8.34 but the ANC value was only 0.504% CCE which was very low and therefore the CFA was not a good liming agent. This CFA is considered as a Class F fly ash which generally has low Ca content.

Heavy Metals and B Concentrations in Soil Solution

Increasing the CFA ameliorant rates clearly reduced the Zn concentrations in soil solution for the ten weeks of incubation (*Fig. 2*). The reduced concentration of Zn probably can be explained by the higher adsorption and precipitation of Zn with an increase in pH (Sims and Kline 1991; Jackson *et al.* 1999). The control treatment (0% CFA) had Zn concentrations in the soil solution ranging from 1.47 mg L^{-1} to

0.67 mg L^{-1} for the four weeks of incubation, increasing drastically at week five to 5.0 mg L^{-1}. It is not known with certainty why there was a delayed dissolution of Zn from the SS. Solution Zn concentrations for the control treatment from week five until week ten of the incubation were still high (> 3.73 mg L^{-1}) compared to other treatments. Treatments using 2.5% and 5% CFA had less than 2.15 mg L^{-1} whereas treatments using greater than 10% CFA had the lowest Zn concentrations which were less than 1 mg L^{-1}. This indicates that CFA is feasible as a stabilization agent to reduce heavy metal toxicity in the SS-treated soil.

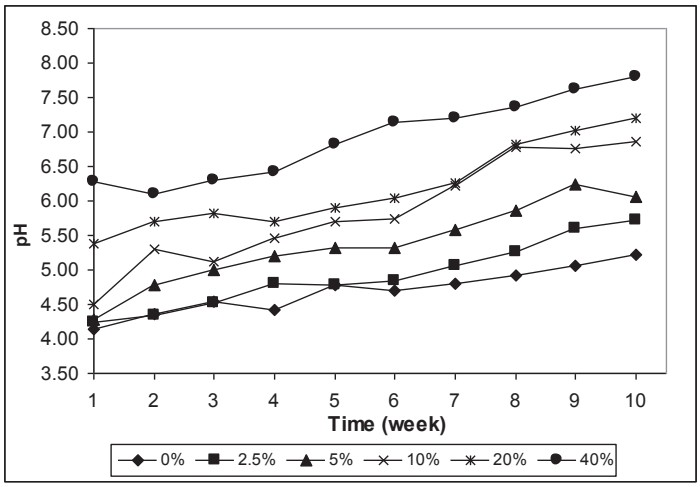


Fig. 1: pH value of soil solution for 10 weeks of sewage sludge and different rates of CFA incubation

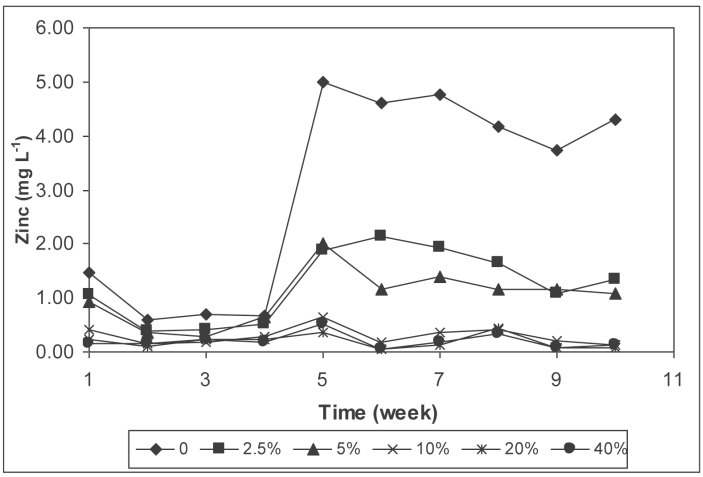


Fig. 2: Soluble Zn for sewage sludge and different rates of CFA treatments

The soluble Cu concentrations in the incubated soil mixture are shown in *Fig. 3*. The results indicate that Cu concentrations in the soil solutions were very low in all treatments including the control which was less than 0.08 mg L^{-1}. The patterns for Cu dissolution over the 10 weeks of incubation were different for each treatment. Copper concentrations increased every week starting from the first week of incubation until week five for the 2.5% CFA treatment, whereas for other treatments, soluble Cu started to drop only after six weeks of incubation. Treatment using 40% CFA showed the highest reading of Cu concentrations (0.08 mg L^{-1}) compared to other treatments.

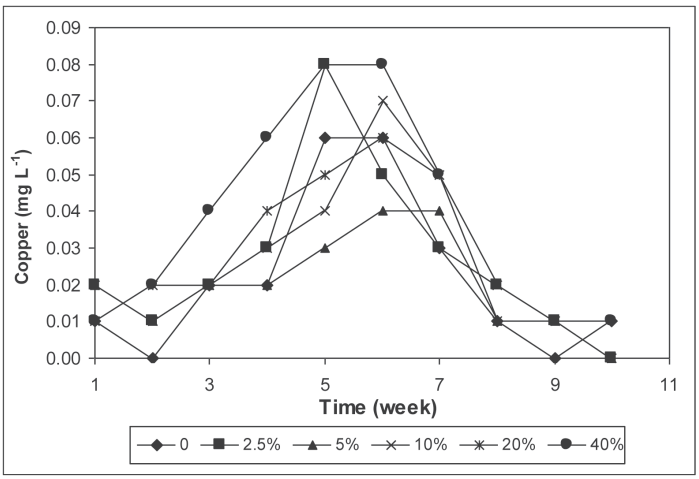


Fig. 3: Soluble Cu for sewage sludge and different rates of CFA treatments

Limitations of CFA for Land Applications

The concentration of B in CFA amended soils appears to be the most serious constrain associated with land application of CFA to soil. Boron concentration especially in unweathered CFA has been reported to be very high and readily available to plants (Adriano *et al.* 2002). Since B is quite water soluble, the weathering of CFA by allowing the adequate drainage should alleviate the detrimental effect of B on plants. The soluble B concentrations in the soil mixture from different rates of CFA are shown in *Fig. 4*. The soluble B concentrations apparently increased with higher CFA rates. Treatment with 0% CFA showed the lowest concentrations of B in the soil solution for the whole period of incubation. As the rates of CFA increased, the soluble B concentrations also increased drastically. The highest B concentration was recorded in the 40% CFA treatment and ranged from 25.68 to 47.65 mg L^{-1} B. It has been reported that most crops require only 0.5 to 1.0 mg L^{-1} of hot water extractable soil B for normal growth, while 5 mg L^{-1} can be toxic for many plants (Ponnamperuma *et al*. 1981; Chlopecka and Adriano 1996). Under field conditions, it might take 3 years to reduce the phytotoxic

effect of B in CFA-treated soil to an acceptable level (Bern 1976). Therefore, it is important to make sure that the CFA is fully weathered before it is be applied as a soil ameliorant.

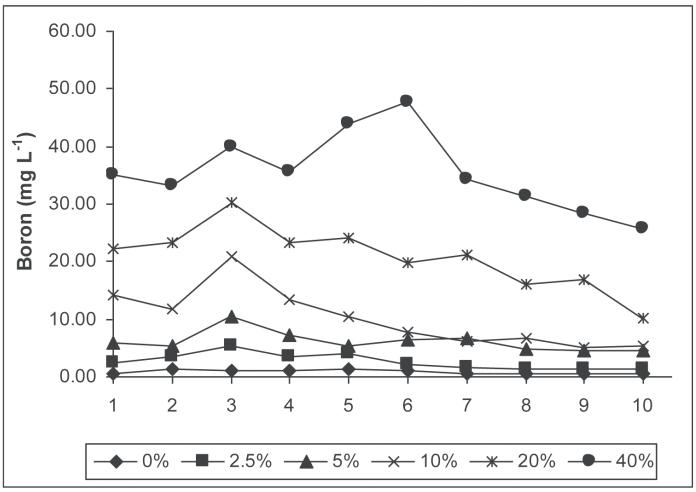


Fig. 4: Soluble B for sewage sludge and different rates of CFA treatments

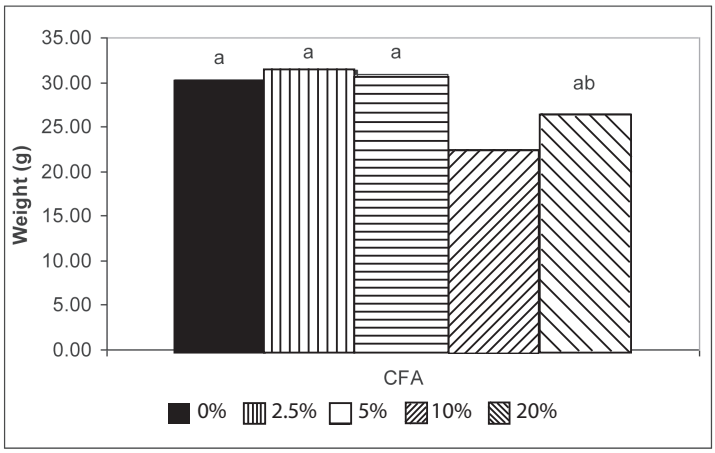
Glasshouse Study

Maize Dry Weight

The dry weight of maize grown in the SS-treated soil with different rates of CFA is shown in *Fig. 5*. There was no reduction in dry weight of maize in soils treated with CFA up to 5% w/w compared to the control treatment. However, addition of CFA at 10% significantly decreased the dry weight of maize compared to the control treatment. Compared to the control, there was no reduction in uptake of macronutrients by maize in all CFA treatments except for N. Thus, the reduction in dry weight might not be due to macronutrient insufficiency. Electrical conductivity (EC), which is a measure of the amount of soluble salts in the soil, was measured to determine the possible presence of salinity problems in the soil due to sludge application. High salinity (> 4 dS m^{-1}) will have an adverse effect on plant growth (Johnson and Fixen 1990). The EC of the control, 2.5, 5.0, 10.0 and 20.0% CFA treatments were 1.41, 2.08, 1.83, 2.56 and 3.52 dS m^{-1}, respectively, and these values were below the soil salinity threshold value of 4 dS m^{-1}.

Maize Nutrient Sufficiency Range for Macronutrients

Concentrations of N, P, K, Ca, and Mg were compared with nutrient sufficiency range (NSR) of maize to assess if CFA application has an effect on the adequacy of macronutrients for plant growth (Table 2). The concentration of N, Ca



Note: Similar letters above the bars indicate that they are not significantly different at 99% confidence level, according to the Duncan New Multiple Range Test (DMRT)

Fig. 5: Dry weight of maize for sewage sludge and different rates of CFA treatments

and Mg were found to be sufficient for maize growth in all the treatments. Phosphorus concentration in CFA amended soil was adequate only at 20% CFA for maize growth. Insoluble forms of P may result due to the high levels of Ca and/or Fe and Al in fly ash (which was not determined in this study), consequently inducing P deficiency in plants. Concentration of K was found to be low compared to the adequate level for maize growth. Hence, additional K (140 kg ha^{-1}) was added after four weeks of sowing to all treatments because visual K deficiency was detected. However, there was no visual P deficiency observed on the maize and therefore no additional P was added. It has been reported that soil P and K deficiencies in maize are exacerbated by fly ash application, probably due to precipitation of soil P (Ponnamperuma *et al.* 1980).

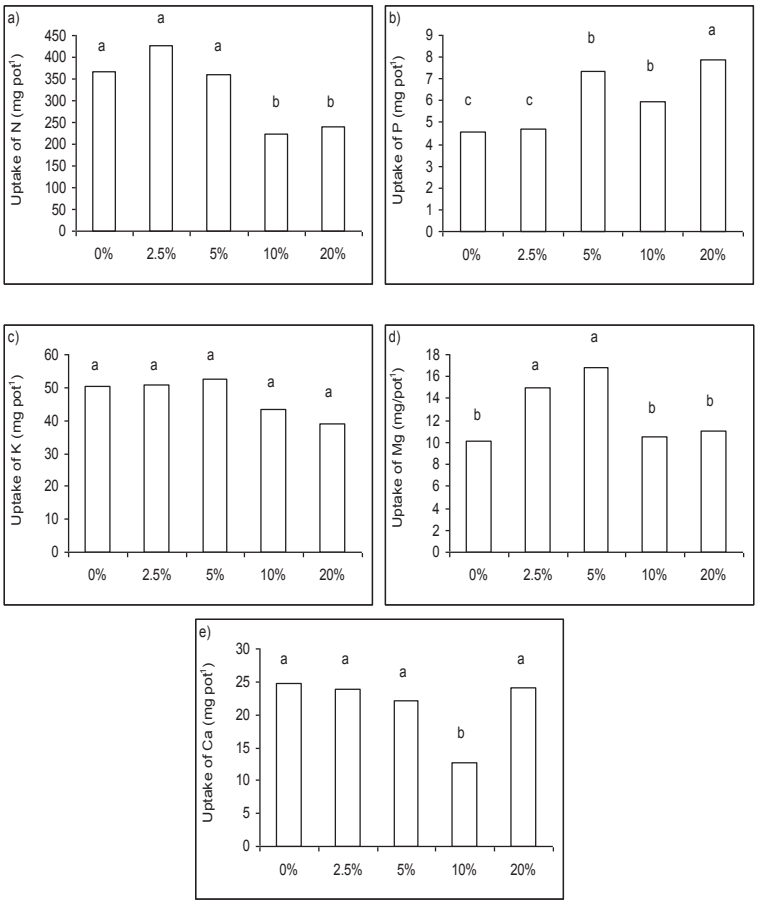
TABLE 2
Comparisons of macronutrients in maize and Nutrient Sufficiency Range (NSR) for maize

Parameter	Rates of CFA					NSR*
	0%	2.5%	5%	10%	20%	(%)
N (%)	12.01	13.72	11.61	9.93	9.11	3.50 -5.00
P (%)	0.15	0.15	0.22	0.27	0.30	0.30 -0.50
K (%)	1.66	1.60	1.70	1.93	2.27	2.50 -4.00
Ca (%)	0.82	0.76	0. 73	0.57	0.91	0.30 -0.70
Mg (%)	0.33	0.47	0.48	0.55	0.71	0.15 -0.45

Note: *Data showed adequate range for maize growth based on Mills and Jones (1996)

Macronutrients Uptake by Maize

The N uptake of maize was not significant between the control and CFA treatments up to 5% CFA (*Fig. 6a*). Application of more than 10% CFA decreased the N uptake by maize. It has been reported that CFA alone was a poor source of N (Bern 1976). The N content for the CFA in this study was only 0.32% (Table 1) which was low compared to the NSR required for maize growth. Hence, the addition of 5% rate of SS as a source of N is required to supply the total crop N requirement for maize growth. A mixture of a large amount of CFA to SS increased the C:N ratio which slowed down the N mineralization process (Zhang *et al.* 2007). This probably explains why the N uptake by maize decreased in the treatment using more than 10% CFA.



Note : Similar letters above the bars indicate that they are not significantly different at 99% confidence level, according to the Duncan New Multiple Range Test (DMRT)

Fig. 6: Uptake of macronutrient (mg/pot) from soil amended with SS and different rates % CFA

The P uptake of maize for soil treated with CFA was significantly higher than the control only at rates of 5% and higher (*Fig. 6b*). However, the concentration of P in the soil mixture receiving 5% CFA was only 0.15%, which was low compared to the adequate level required for maize growth. This clearly showed that P uptake by maize was not from CFA, since CFA was a poor source of P. The addition of CFA mixtures to the SS-treated soils at 5% and 10% CFA significantly improved the P uptake of maize as compared to the control. However the usage of the highest amount of CFA (20%) gave the highest P uptake of maize (7.90 mg/pot).

As shown in *Fig. 6c*, there was no significant difference in potassium (K) uptake by maize using CFA mixture compared to the control (0% CFA) since there was only 0.34% K in this CFA (Table 1). The concentration of K in the soil mixture was low compared to the adequate level for maize growth indicating that CFA application has no effect on K uptake by maize.

The Mg uptake of maize for treatments using 2.5 % and 5% addition of CFA were found to be significantly higher compared to the control treatments (*Fig. 6d*). However, the addition of more than 10% CFA significantly decreased the Mg uptake of maize as compared to the treatments with lower rates of CFA. It was found that the 0.44% of Mg content in this CFA was within the adequate amount for maize growth. This indicates that CFA can be a source of Mg; however the right proportion of CFA should be used to supply an adequate amount of Mg for maize growth. In general, there was no significant difference in Ca uptake of maize between the control and CFA treatments except for the 10% CFA which showeda lower Ca uptake (*Fig. 6e*). This shows that addition of CFA as soil amendment did not increase Ca uptake by maize even though the concentration of Ca in this CFA was 0.97 %, which falls within the adequate level for maize growth. This suggests that CFA can be a good source of Ca but a proper amount should be added to avoid the Ca and Mg imbalance.

Maize Nutrient Sufficiency Range for Micronutrients

For the micronutrients sufficiency range, only Zn and Cu data were available for maize growth (Table 3) (Schumann and Sumner 1999). Concentration of Zn was found to be higher than the sufficiency range for maize growth in <10% CFA tteatments and might cause Zn toxicity in maize especially in <5% CFA treatments. Copper concentrations in all treatments were also found to be within the adequate level for maize growth.

Heavy Metals Uptake by Maize

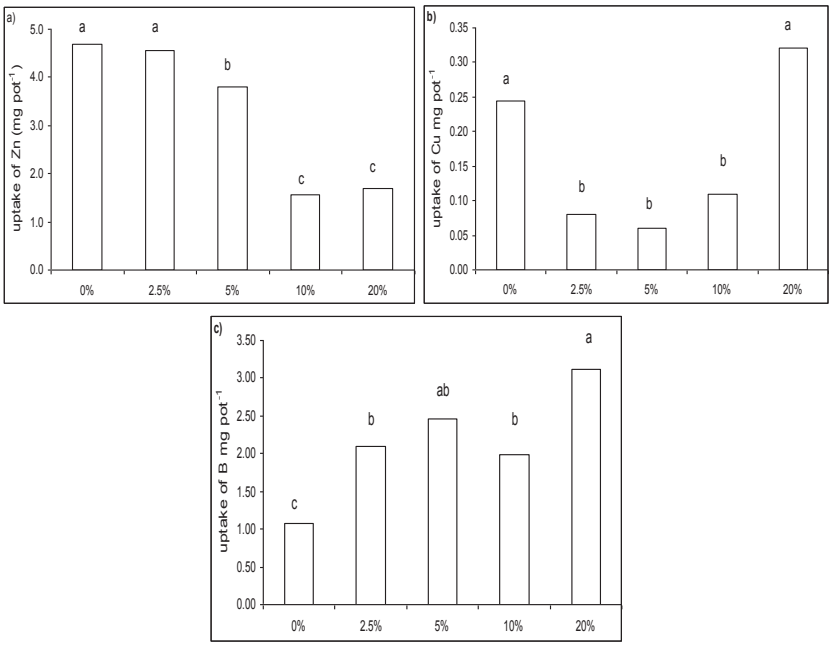
The Zn uptake by maize for treatment using CFA is shown in *Fig. 7a*. Overall, the concentration of Zn uptake by maize significantly decreased at higher rates of CFA treatments. Usage of 2.5% CFA did not show any significant result as compared to the control treatment. However, the addition of more than 5% CFA significantly reduced Zn concentration in maize. This shows that the CFA is useful as a soil amendment to fix Zn in the SS-treated soil.

TABLE 3
Comparisons of micronutrients in maize and Nutrient Sufficiency Range (NSR) for Maize

Parameter	Rates of CFA					NSR*
	0%	2.5%	5%	10%	20%	(mg/kg)
Zn (mg/kg)	153	129	101	67	43	20 - 60
Cu (mg/kg)	8.0	2.7	2.0	5.3	12.0	5 - 20
B (mg/kg)	36	66	81	88	120	n.a.

n.a. – data not available;

Note: * Data showed adequate range for maize growth based on Mills and Jones (1996)



Note : Similar letters above the bars indicate that they are not significantly different at 99% confidence level, according to the Duncan New Multiple Range Test (DMRT)

Fig. 7: Uptake of heavy metals and B (mg/pot) from soil amended with sewage sludge and different rates % CFA

The results showed that application of CFA up to 10% reduced Cu uptake by the maize plants compared to the control *(Fig. 7b*). However, there was no significant difference in Cu uptake by maize between the control and the 20% CFA treatment indicating that CFA can be beneficial as a soil ameliorant to reduce Cu uptake by plants but, the amount of CFA should be applied at a proper rate to avoid Cu toxicity.

Limitations of CFA for Land Application

The most common adverse effects of using CFA as a soil amendment is the high content of phytoavailable boron (B). A concentration of 11 mg kg^{-1} in maize tissue is reported as the lowest sufficiency level for maize (Mills and Jones 1996), while 98-100 mg kg^{-1} is reported to cause toxicity to the maize plants (Jones *et al*. 1990). Only the highest treatment of CFA (20%) exceeded this threshold level with a mean concentration of 120 mg kg^{-1}. *Fig. 7c* shows B uptake by maize at different rates of CFA treatments. The B concentration apparently increased with the usage of higher CFA rates. Application of CFA at all rates increased B uptake by maize; however they were all below the threshold level of 100 mg kg^{-1} with the exception of CFA at 20%. This trend shows that CFA can be applied as a soil amendment; however it should not be applied excessively to avoid the phytotoxic effect of B. It is also important to make sure that the CFA is fully weathered before it is applied as a soil ameliorant.

CONCLUSION

The amount of major macronutrients in the CFA is considerably low for plant growth and therefore this byproduct cannot be a good fertilizer supplement if it is used alone. The CEC value of the CFA was low and the pH value was alkaline. Usually an alkaline agent can be used as a stabilizing agent to reduce pathogen and heavy metals availability in SS. However, this CFA was not a good liming agent, since the CCE was low. All the heavy metals in CFA with the exception of B were within ranges found in most soils and the allowable level for land application of a waste byproduct. When mixed with sewage sludge, all the macronutrients were sufficient for maize at the treatment rates given, with the exception of P and K. Toxic levels of B were detected in the foliar tissues of maize at the highest rate (20% w/w) of CFA addition. Coal fly ash can significantly reduce the Zn derived from sewage sludge from being taken up by the maize plants at a ratio of 2:1 (10%:5%) and up to the ratio of 4:1 (20%:5%) coal fly ash to sewage sludge. However, the role of organic matter in sewage sludge in slowing down Cu and especially B uptake by the maize plants was not apparent in this study.

This study indicates that land applications of CFA can be recommended as soil ameliorant because of their effectiveness in reducing heavy metals in the SS-treated soil probably due to the increase in soil pH. However, the CFA must be applied at a correct dose and has to be weathered or lagooned to remove excess B before it can be used as a soil ameliorant. Hopefully, this research can be used as a guideline on the utilisation of CFA as a soil ameliorant for crop production in tropical acid soils.

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