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SUITABILITY OF MORUPULE FLY ASH AS AMENDMENT FOR TWO AGRICULTURAL SOILS IN BOTSWANA

by

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Abstract

Electricity generation in thermal power stations results in high fly ash production that, if not managed properly, will be a potential source of pollutants. In Botswana, the fly ash from Morupule Power Plant is being used as an amendment for agricultural soils through a series of experiments that characterized and assessed fly ash deposits as liming material and nutrient source; assessed the effects of fly ash amendments applied at different rates in combination with the nutrient sources on the growth, yield, and quality of harvested spinach, rape, and corn successively grown in two representative soils as well as their effect on soil properties and heavy metal availability.

Chemical characterization of Morupule FA showed to have an alkaline pH of 8.12 to 8.42, an EC of 2300 to 2370 mS/m, very low organic matter contents of 0.012%, and a liming potential equivalent to 98% CaCO_3 . It contained high concentrations of essential elements for plants such as P (865 mg kg^{-1}), K (1676 mg kg^{-1}), S (34472 mg kg^{-1}), Ca ($119230 \text{ mg kg}^{-1}$), Cu (23 mg kg^{-1}), Fe (36222 mg kg^{-1}), Mn (796 mg kg^{-1}), Ni (66 mg kg^{-1}), Zn (32 mg kg^{-1}). It also contained some non-essential elements for plants such as As (11 mg kg^{-1}), Hg (8.6 mg kg^{-1}), Ba (614 mg kg^{-1}), Cr (159 mg kg^{-1}), Sr (535 mg kg^{-1}), Zr (374 mg kg^{-1}), and Pb (51 mg kg^{-1}).

In Selebi Phikwe soil, the yield of spinach, rape, and corn was increased due to the addition of FA at the rate of 5 to 15%. These yields were enhanced by the addition of compost and NPK, or its combination, especially in treatments with 10% FA. For spinach, treatments with 10FA+comp, 10FA+NPK+Compost, and 15FA+compost had heavy metal concentrations below the maximum allowable limit (MAL) for human consumption; while for rape, only the treatment

of 10FA+compost had heavy metals concentrations below MAL. While the kernels harvested from 10FA+compost had heavy metal concentrations below the MAL. FA increased the pH, reduce heavy metal availability, and increased the amount of available nutrients of Selebi-Phikwe soil.

In Tswapong soil, the highest dry matter yield of spinach and rape was obtained in 10FA+NPK+compost, and in 5%FA+NPK+compost for corn. Among the different treatments, spinach and rape grown in 10%FA+NPK alone or combination with compost; and corn kernels from treatment with 15%FA + Compost alone or combination with NPK had low heavy metal concentration, which are below the MAL. FA amendments increased the pH up to 8.0 and modify the heavy metal and nutrient availability of neutral Tswapong soil.

Overall, the application of FA from 5% to 15% enhanced the growth of spinach, rape, and corn grown in Selebi Phikwe and Tswapong soils. For this study, the optimum FA rate was 10% FA which gave the highest dry matter yields for the series of crops grown in Selebi Phikwe and Tswapong soils with minimum heavy metal accumulation in harvestable parts of the crops.

Keywords: *corn, fly ash amendments, heavy metal availability, nutrient sources, rape, spinach*

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Chapter 1

Introduction

1.1 Background of the study

Combustion process of coal in thermal power plants produces fly ash as a waste product discharged in ash ponds and lagoons. Fly ash disposal in open space such as lagoons, is a global environmental concern because it is a potential source of pollutants such as heavy metals. Continuous generation of fly ash converts arable and pastoral land into ash landfills and lagoons, consequently leading to the contamination of soils, water, air and vegetation (Pandey., 2012). Therefore, there is a need to find alternative use of fly ash in other areas such as in agriculture (Pandey., 2019).

In Botswana, Morupule Power station is responsible for coal combustion and generates fly ash in the process. Morupule "A" Power Station, with a capacity of 132 MW (33 MW*4 Units), is currently Botswana's sole source of base load power (Likuku et al., 2013). Coal in Botswana is semi-bituminous with relatively high percentages of ash (20%) and Sulphur (1-2%). The projected coal reserves in Botswana are 212 billion tons, implying that coal combustion processes will generate enormous amounts of fly ash (Gajaje et al., 2021). A total of 240 tons of fly ash are produced per day (Gajaje et al., 2021). Hence, the proper disposal of waste fly ash is a major priority for Botswana Power Corporation (BPC).

Bulk volumes of fly ash are difficult to manage in developing countries like Botswana. As a result, storage of FA on dumpsites requires high operational cost especially in the monitoring of its environmental impacts and prevention of the spread of pollution to adjacent environment (Gajaje et al., 2021). Several options are undertaken by some group of researchers to manage FA

disposal that include developments of phytoremediation strategy to extract heavy metal contaminants and phytostabilization of fly ash ponds to mitigate contamination (Ultra., 2020; Manyiwa and Ultra., 2021). Fly ash has dominantly been utilized in construction industry as a soil stabilizer for pavement and road embankments and a component in brick molding (Adewuyi and Mojakgesa., 2020). The enhanced utilization of fly ash will convert waste into a useful resource, thus solving the waste disposal challenge to some degree and conserve resources and the environment.

1.2 Statement of Problem

Current waste management practices for Morupule fly ash have the potential to generate environmental risk and health hazard especially in adjacent areas. The use of fly ash as an amendment for agricultural soils with acidity and nutrient deficiency problems could therefore be explored as a management alternative. However, depending on the properties of the fly ash, several draw backs may occur that can change some physicochemical properties of the soil permanently when used as soil amendments. Therefore, there is a need to evaluate Morupule fly ash physiochemical properties, their effects on soil nutrient availability and dynamics, heavy metal availability and translocation from the soil to plants, soil quality indexes and product quality. Similarly, there was no previous study conducted to assess the suitability of Morupule fly ash as amendments to soil devoted to crop production in Botswana.

1.3 Aims and objectives

The overarching aim of this study is to assess the potential of fly ash as a safe and suitable amendment in two (Selebi Phikwe and Tswapong) agricultural soils. The specific objectives are:

Specific Objectives:

1. To characterize Morupule fly ash deposits based on their physical and chemical properties
2. To assess the effects of different rates of fly ash application in combination with different nutrient sources; no fertilizer (-NF), compost (+COMP) at 20-ton ha⁻¹ (123g pot⁻¹), NPK (+NPK) (120-90-60kg ha⁻¹) and a combination of 10 tons ha⁻¹ (half) compost and NPK at 60-45-30 kg ha⁻¹ (+COMP+NPK) on the growth and quality of harvested spinach, rape and corn.
3. To assess the effect of different rates of fly ash amendments in no fertilizer (-NF), compost (+COMP) at 20- ton ha⁻¹ (123g pot⁻¹), NPK (+NPK) (120-90-60kg ha⁻¹) and a combination of 10 tons ha⁻¹ (half) compost and NPK 60-45-30 kg ha⁻¹ (+COMP+NPK) on soil properties and heavy metal availability.

1.4 Significance of the study

Morupule fly ash could be a useful resource for the amendment on acidic and nutrient deficient soils. The use of fly ash as a soil amendment has potential to convert waste into a useful resource in agriculture. The output of the study will be a comprehensive data on the safe utilization of fly ash as a soil amendment for agricultural purposes. Thus, the Ministry of Agriculture (MoA) will have a guide on how fly ash can be used on agricultural soils in Botswana, and this will enhance safe utilization of fly ash from Morupule in the agricultural sector. The results will also help the farmers to access alternative, cost-free and readily available resources that will improve farm productivity and contribute to food security in Botswana. Specifically, appropriate data on the levels of fly ash application on crops and the quality of the produce grown in fly ash will be generated and will serve as a guide for future recommendations. Moreover, when fly ash is

eventually used as amendments in agricultural soils, it will be an avenue for safe management of fly ash from the power plants and consequently conserve resources and preserve the environment.

1.5 Scope of the study

The study utilizes pot experiment but does not involve field experiment. The study used a series of experiments to assess the medium-term effect of fly ash on growth, yield, quality of harvest based on heavy metal contents, and changes in soil properties under screenhouse conditions. Therefore, the results obtained should be treated with caution for it does not necessarily reflect field conditions.

Chapter 2

Literature Review

2.1 Fly ash generation and properties

Morupule Power Station generates approximately 1000 GWh of electricity per annum (Gajaje et al., 2021). Botswana has approximately 212 billion tons of coal reserves, which equates to the large amounts of fly ash produced at a rate of 102 000 tons per year (Central Statistics Botswana 2000). Coal in Morupule consists of high calorific bitmus coal. The ash yield and sulfur in Morupule are about 20% and 1.2% respectively (Zhai et al., 2019). Naturally, fly ash contains toxic heavy metals such as Cr, Zn, Cd, Ni, Pb, and Cr (Rautray et al., 2003; Panda and Biswal., 2018) with low nitrogen and phosphorus. Morupule fly ash is alkaline with a pH of 8.8 (Manyiwa et al., 2021). This is similar to the fly ash pH range from other countries which are between pH 4.5 and 12 (Ukwattage et al., 2013). Chemically, fly ash consists of Si, Al, Fe, Ca, Mg, Na, and K forming the major matrix but does not contain C and N due to high combustion temperature.

2.2 Impacts of fly ash amendments on soil bio-physicochemical properties

2.2.1 Texture

The texture of the soil can be changed by adding the appropriate amount of fly ash. The addition of 70 tons of fly ash per hectare changed the texture of sandy and clayey soils to loamy soil in a field experiment (Gupta et al., 2002; Fail and Wockhock, 1977). The predominance of silt-sized particles in fly ash is responsible for the change in soil texture. The average silt-sized content in fly ash is about 63.2% (Sharma, 1989; Tejasvi and Kumar, 2012).

2.2.2 Soil structure, water holding capacity and porosity

Aside from soil texture, the application of fly ash soil has the potential to increase soil porosity and improve water retention capacity (Sahu et al., 2017). The addition of appropriate amounts of fly ash can modify the soil physical characteristics because of the silt size particles and calcium content (Ukwattage et al., 2013). Application of fly ash up to 50% to Ultisols changed the microaggregate size distribution of soil but not on soils with high organic matter and free iron oxide contents (Lu and Zhu, 2004). Fly ash application also increased the water holding capacity of soils and reduced the density (Kohli and Goyal, 2010). Similarly, the addition of fly ash to soil increased the water retention capacity by 50% compared to the pure soil due to the fine textured substrates that hold more water than coarse textured substrates (Gangloff et al., 2000; Sighn and Kansal, 1994). Also, the addition of 10% FA increased available water holding capacity to plants by 52 and 124% over the control respectively for sandy loam and sandy soils. Naturally, fly ash is ineffective at retaining water, but it significantly increases the water holding capacity of the soil mixture (Chang et al., 1997).

2.2.3. Soil pH

Soils with toxic pH can be supplemented with amendments as buffering agents that could neutralize their pH and maximize the nutrient availability. Previous studies showed that the fly ash addition increased the pH in acidic soils (Pandey et al., 2002; Tejasvi and Kumar, 2012). The rapid release of Ca, Na, Al, and OH ions from the fly ash causes the initial increase in soil pH after the addition of alkaline fly ash (Tejasvi and Kumar, 2012; Wong and Wong 1990). According to Shaheen et al. (2014), the addition of fly ash to the soil increased the soil's buffering capacity for pH restoration. Most of the fly ash produced around the world is alkaline, hence, the application

of fly ash increases the soil pH (Kumar et al., 2000). Fly ash's ability to neutralize acidic soils is one of its most useful properties (Tejasvi and Kumar, 2012; Tejasvi and Kumar, 2012; Jastrow et al., 1979). Experiments with calcareous and acidic soil showed that fly ash addition increases the pH of the former from 8.0 to 10.8 and of the later from 5.4 to 9.9 (Page et al., 1979; Tejasvi and Kumar, 2012). Sahu et al., (2017) conducted experiments using acidic soils and noticed a pH increase from 5.3 to 6.0 in acid lateritic soil with addition of fly ash at 10 tons/ha. However, excessive quantities of fly ash to alter pH can cause permanent increase in soil salinity due to increase in soluble salts especially with unweathered fly ash (Gupta et al., 2002). The key microorganisms that perform N fixation and other important processes for plant growth are endangered by the elevated pH caused by the alkaline nature of fly ash. However, the long-term impact of the application of fly ash changes in soil pH require further investigation.

2.2.4 Electrical Conductivity

The application of fly ash significantly increases the electrical conductivity of the soil mixture by increasing the levels of soluble major and minor inorganic constituents (Qaswar et al., 2020; Gupta et al., 2002). Kalra et al. (2000) obtained an 11.7% increase in EC with soil- ash mixture compared to soil alone. The electrical conductivity reflects the total concentration of soluble cations and anions, and it is positively correlated with pH (Basu et al., 2009). However, it can also be influenced by moisture content, texture, and soil temperature.

2.2.5 Nutrient availability

Fly ash can help enhance the soil's nutrient status if added appropriately (Basu et al., 2009). The readily available lime in fly ash reacts with acidic elements in soil to release nutrients like S,

B, and Mo in the form and amount that crop plants require. On the other hand, fly ash application will increase activity of ionic transporters in the roots that may be responsible for the increased accumulation of principal ions such as Zn, Mn, and Cu by the paddy shoot/ grain due to higher essential ion availability in fly ash (Gupta, 2016). The application of fly ash resulted to the accumulation of Mn, Zn, Cu, Ni, Cr, Pb and Cd in plant tissues within plant tolerance limit (Jambhulkar and Juwarkar, 2009). A study conducted using *Beta vulgaris*, observed an increase in the concentration of heavy metals (Cu, Zn, Cd, Ni and Cr) with an increase in the application of fly ash indicating the potential of fly ash as source of heavy metals (Singh et al., 2008). Pandey et al., (2009) found that the application of fly ash to agricultural soils increased the Ni uptake, while Cr and Cu concentration reduced in *Vicia faba*. For *Cajanus cajan*, application of fly ash at 25% (w/w) resulted to safe concentration for human consumption (Fe, Zn, Mn, Cr, Cd, Pb, B, Al, Mo and Ni) in the edible parts. Combined application of fly ash and manure slightly increased the concentration of B, Mn, Se and Zn in plant tissues while the application of fly ash from 5%, 10% and 20% enhanced the growth of alfalfa, however the application at 40% (w/w) inhibited the shoot growth and slightly inhibited the root growth (Pandey and Singh, 2010). This is primarily due to the high concentrations of dissolved salts in fly ash, which hinder plant growth at higher application rates. Clearly, fly ash application or in combination with other materials will influence nutrient availability and uptake by plants including the non-essential elements that may be present in fly ash or in soil.

2.2.6 Heavy metals availability

Morupule Fly ash applied to mine tailings has increased the pH of the mine tailings, reduced the availability of Cu, Ni, Pb, Mn and Zn and consequently reduced the concentration of

these metals in shoots several plant species including three *Acacia sp.* and *D. regia* (Ultra and Manyiwa et al., 2020; Ultra et al., 2020). Similarly, Saffari et al., (2018) showed that fly ash added into heavy metal contaminated soils yields the highest dry matter yield in corn and reduced the availability of heavy metals. This was attributed to the ability of fly ash to increase the specific surface area, increase CEC and pH. Such phenomenon promotes heavy metals' sorption in the soil through surface complexation and ion exchange mechanisms. In addition, from the same experiment, fly ash has significantly decreased mobility factor of heavy metals and its phytoavailability.

When fly ash was combined with biochar, a synergistic effect reduced the metal availability due to surface functionalization and complexation and consequently enhanced the maize biomass yields. The combined application also influenced the transfer rate and translocation in plant by metal stabilization process (Munir et al., 2020). Modified fly ash also significantly enhances the stabilization of cadmium and lead (Xu et al., 2021).

2.3 Biological properties of soil

Factors such as salinity, toxicity of other trace elements, and poor physical conditions can limit microbial activity when using fly ash as a soil additive (Pandey and Singh., 2009). However, the ultimate restricting cause for microbial activity is frequently a lack of carbon as a source of energy for heterotrophic microbes and insufficient nitrogen supply (Pandey and Singh., 2009). Pandey and Singh, 2009 suggested that microbial population and diversity was enhanced by nutrient accumulation. According to Karpagavalli and Kamabadrn, (1997) the application of fly ash reduced the growth of several soil-borne pathogenic microorganisms. The increase in pH and electrical conductivity (EC) due to fly ash Pandey and Singh, (2009) might also inhibit microbial

activity. Previous studies noted that an increase in enzyme activity, and CO₂ evolution in soil encouraged soil microbial activity. Enzyme activity (invertase, amylase, dehydrogenase, and protease) increase with the addition of 10tons/ ha of fly ash but reduce with addition of rates of fly ash (Sarang et al., 2001). With the addition of fly ash at 5% (w/w), there is a significant stimulation of soil respiration and microbial activity with the help of earthworms (Sahu et al., 2004). This is due to induced substrates that produce earthworms. Pandey and Singh (2010) reported that the combined application of fly ash with the help of earthworms at lower rates stimulates soil biological activity and improves nutrient cycling in acidic soils. The combined use of fly ash and manure has been shown to increase the growth and activity of microorganisms in acid soils (Pandey and Singh, 2010). Boron toxicity is a major concern with fly ash as soil amendments due to induced inhibition of microbial respiration (Jala and Goyal, 2004). As fly ash weathers and nutrients build, microbial activity and diversity increases (Jala and Goyal, 2004).

2.4 FA as the source of essential nutrients and its effects on the growth of crops

Fly ash contains essential minerals like iron (Fe), zinc (Zn), copper (Cu), molybdenum (Mo), and boron (B,) and macro nutrients like potassium (K), phosphorus (P), calcium (Ca) and potassium (K), essential to plant growth, and other elements such as B, Se, and Mo and metals that can be toxic to the plants. Fly ash also has liming substances that readily reacts with acidic components in soil leading to the release of nutrients such as S, B and Mo in the form and amount favorable to plants.

2.5 Potential drawbacks using FA and their effects on crops and soil

The environmental impacts of fly ash have been fully noted due open land disposal method. The massive accumulation and disposal of fly ash causes soil degradation and poses a threat to human health. Because fly ash particles are small enough to evade emission control devices and float in the air, they have become a major source of air pollution. Furthermore, fly ash can reach sub soil and cause siltation, clog natural drainage systems and contaminate groundwater with heavy metals (Yao et al., 2014). Fly ash contains a significant amount of trace elements (Yao et al., 2014). Plants have a variety of intracellular sites or metabolism that are sensitive to metal ions. These may easily be harmed by the addition of synergistic effects of various toxic metals found in fly ash (Gupta et al., 2000; Woolhouse, 1983). Fly ash contaminates the soil, surface, and groundwater because of its water-soluble components (Choi et al., 2002). Metals such as V, Cr, Ni, Cd and Pb are potential environmental hazards even at low levels (Nyale et al., 2014). Fly ash is a potential radioactive material, however, the exposure from fly ash depends on the parent coal and combustion remains. The radioactive contaminant elements in fly ash include Ruthenium ^{222}Ru and Ruthenium ^{220}Ru . Uranium (U), Thorium (Th), and decay products are liberated from the coal matrix during the combustion process and circulated across the gas and solid phases (Mahur et al., 2009; Yao et al., 2014).

2.6. Status of Crop Productivity in Botswana

The Agricultural sector in Botswana includes dryland crop production. Traditional farming is the most dominant in terms of numbers of people involved and the geographical coverage (Gases, 2012). The majority of farmers are small-scale farmers who typically need continued assistance in capacity building to commercialize agriculture. Poor soil fertility remains a major

challenge in most soils in Botswana that leads to crop yields of less than one tonne per hectare for main staple grains. Lack of knowledge on the use of fertilizers and application rates also hamper dryland crop production are among the reasons. Therefore, technologies and software's should be availed to help assist farmers. Additionally, these limitations are worsened by poor socio-economic infrastructure in continental Africa (Wani et al., 2009).

Chapter 3

Materials and Methods

3.1 Site Description and Collection of soil and Fly Ash

Representative agricultural soils were collected from Selebi Phikwe and Tswapong (see Figure 3.1). The soils from Selebi Phikwe represents the vast agricultural areas that are influenced by mining activities in Botswana (Manyiwa et al., 2022). The farm site where the soil was collected is about 10 kms away from the Cu- Ni Mine along Mmadinare road (Fig. 3.1). The Cu- Ni mine has over the years extracted and processed Cu and Ni. The processes of the BCL mine resulted in the production of a huge amount of mine tailings, slags, and smelter stack which are poorly managed. Manyiwa et al., (2021) indicated that waste has resulted in the pollution of the areas. The soils in Selebi Phikwe are dominantly Eutric Regosols and Haplic Luvisols (Likuku et al., 2013). The representative agricultural soil from Tswapong belongs to Tswapong soils. These are predominantly agro-pastoral soils but urbanizing region in the Serowe-Palapye sub-district in the Central District of Botswana. Palapye soil is predominantly Arenosols and underlain by meta-sedimentary rocks overlaying Basement Complex rocks, comprising mainly of quartzites, shales, siltstone, sandstones which form part of the Tswapong Hills (Akinyemi et al.,2021).

The fly ash was collected from the dumpsite of the Morupule B power plant (latitude 24° 30' and 24° 31' S and longitude 27° 02' and 27° 03' E) which is located 5 km away from Palapye and 30 km away from Serowe laying on the south of A14 main road (Palapye- Serowe road, Fig. 3.1). On the other hand, the compost (Cultera Kompos[®]) was acquired in an agricultural supplies shop in Palapye, Botswana. The soils for the experiments were collected at a depth of 10 cm and sieved using 2mm sieve to remove undecomposed organic matter materials and debris. Fly ash was taken

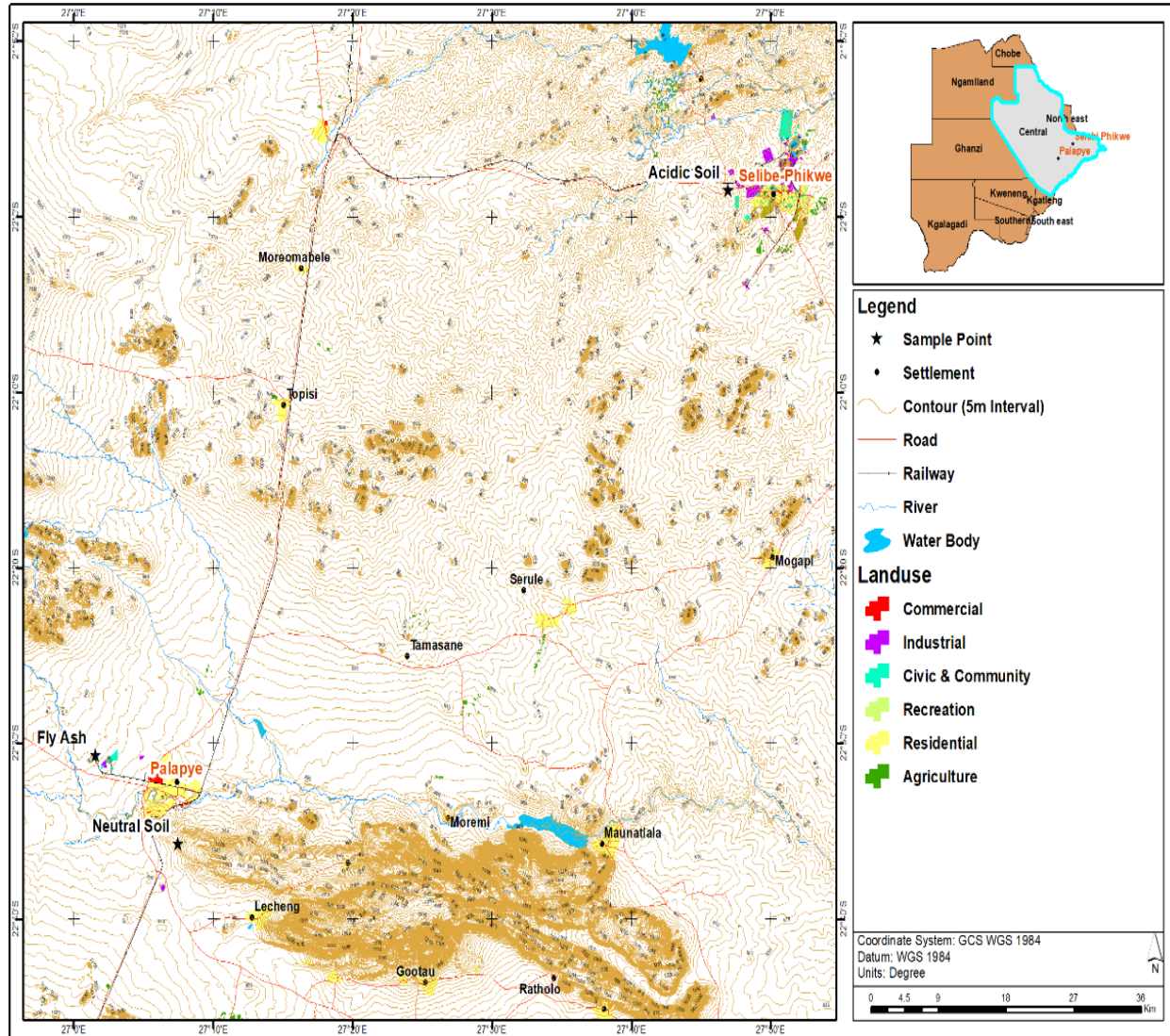


Figure 3.1. Map showing study area and sampling of soils and fly ash

from the center of the dumpsite, sieved, and stored in containers pending use.

3.2 Chemical Characteristics of Soils, Fly Ash, and Compost

The chemical properties and heavy metal contents of the soil, fly ash, and compost were gathered before commencing the experiment using the standard procedure outlined by Ultra

(2020). The pH and EC of the soils, fly ash and compost were measured using a portable pH meter with soil: water suspension (1:2), and organic matter content expressed in percentage was measured using the loss on ignition method. A wet- acid digestion method using a Microwave digester (Ethos Easy, Advanced Microwave Digestion System) was used to determine the heavy metal concentrations of the soils, fly ash and compost.

3.3 Liming Potential of Fly Ash

The liming potential of fly ash was determined by the calcium carbonate equivalent in a back titration method. The liming equivalent was calculated for Selebi Phikwe soil. Briefly, the back titration method was carried out by mixing 5g of fine crushed fly ash into conical flask, 10 mL of 1 N HCl and 50 mL distilled water, heated until boiling for 2 mins. The mixture was left to cool, and 3 drops of phenolphthalein indicator were added and titrated against 1 N NaOH. Then, the percent calcium carbonate was calculated using the following equation:

$$CaCO_3(\%) = \frac{[(Vol.HCL \times Vol.NAOH \times IN)]}{1g} 5$$

To determine the liming requirement of Selebi-Phikwe soil using fly ash, a soil-fly ash incubation study was conducted. Briefly, fly ash was added at the rate 0g, 10g, 25g and 50g per 1000g of soil in a 1 L glass bottles. The soil-fly ash mixture was thoroughly mixed, and the moisture content was adjusted to 80% filed capacity by adding distilled water. The mixtures were incubated for a period of 3 months while monitoring the changes in soil pH over time. The bottles were opened for a few hours each day to facilitate gas exchange. The Soil pH at a 1:2.5 soil: water ratio was measured in four different treatments, including the control (0% FA) at 9, 30, 60, and 90 days after beginning the incubation period to ensure the equilibrium pH was reached. The fly ash

application rates were plotted against pH of the soil to estimate the amount of FA needed to raise the soil pH of Selebi-Phikwe soils.

3.4 Preparation of Pots and Treatment description

The experiment was conducted in 10 L plastic pots (28.0cm top diameter, 24.0 cm base diameter, and 22.5 cm height) and kept under screen house conditions. The experiments used a 2-factorial with three replications arranged in a complete randomized design. Factor 1 consist of 4 rates of fly ash application and factor 2 consist of 4 types of nutrient sources comprising the 16 treatment combinations which were administered in both the Selebi-Phikwe and Tswapong soils (see Table 3.1). The application rates of fly ash were 0%(0%FA), 5%(5%FA), 10% (10%FA) and 15% (15%FA) by weight basis and the four types of nutrient sources are: no fertilizer (-NF), compost (+comp) at 20- ton ha⁻¹ (123g/ pot), inorganic NPK (+NPK) at 120- 90- 60 kg ha⁻¹ and a combination of 10 tons ha⁻¹ compost+ 60- 45- 30 NPK kg ha⁻¹(+NPK+ comp). A total of 48 pots were used for the study, of which 12 are pure soil, while the remaining 36 contained 5%, 10%, and 15% FA at 12 pots for each FA rate. The different nutrient sources were applied accordingly: for the control, no fertilizer was added; for the treatments with compost, the compost was mix thoroughly into the soil in each pot at 123 g pot⁻¹ for full rate and 62 g pot⁻¹ for half rate; for treatments with inorganic NPK, the fertilizer in the form of compound granulated NPK (Omnia Nutrinology) with fertilizer grade of 2.3.2 (22) was added at 5.9 g pot⁻¹ plus 1.32 g of limestone ammonium nitrate (LAN), which contains 28 % N for the full rate while 2.95 g pot⁻¹ of granulated NPK plus 0.65 g pot⁻¹ of LAN for the half rate. The rate of FA, compost and NPK application was based on the soil test value initially done in the study and based on the fertilizer recommendation for these crops in Botswana. These nutrients sources were mixed for each designated pot and

incubated for 2 weeks before planting. The complete treatment description is presented in Table 3.1.

3.5. Plant Establishment and Growth and Yield Monitoring

Spinach was planted as the first crop, rape as the second and corn as the third, sequentially in both soils. The experiments were conducted for 58 weeks from the time of planting of pre-germinated seeds of spinach until the harvest of the corn. For plant establishment, the seeds were soaked in water for 24hrs and incubated in a sterile Petri plate lined with moistened filter paper until the radicle emergence. Uniformly pregerminated seeds were selected and transplanted to already prepared pots at 10 seeds per pot. Two weeks after sowing, the seedlings were thinned to 3 plants per pot and maintained for 40 days before harvest for both the spinach and rape respectively and about 3 months for corn. The growth was monitored until harvest. After the harvest of spinach, the soil was mixed thoroughly and rested for 2 weeks before the establishment of rape in the same treatments following the same procedure described for spinach. The corn seeds were planted after harvesting rape (second crop) and was harvested after 60 days. The cropping sequence on the same media was adapted in order to cover several crops that are commonly grown in Botswana and at the same time to be able to monitor the medium-term impact of FA amendments on soil properties. The experiment was carried out in BIUST's screenhouse in a semi-arid climate with annual rainfall ranging from 129 to 988 mm, with an average of 396 mm (Zhai et al., 2009).

Table 3.1. Description of the 16 treatments from the combination of different rates of fly ash application and 4 types of nutrient sources.

Treatments	FA Level	Nutrient source	Treatments	FA Level	Nutrient source
T1	0% FA	Control (-NF)	T9	10% FA	Control (-NF)
T2		Compost (+COMP)	T10		Compost (+COMP)
T3		NPK (+NPK)	T11		NPK (+NPK)
T4		NPK+ compost (+NPK+COMP)	T12		NPK+ compost (+NPK+COMP)
T5	5% FA	Control (-NF)	T13	15% FA	Control (-NF)
T6		Compost (+COMP)	T14		Compost (+COMP)
T7		NPK (+NPK)	T15		NPK (+NPK)
T8		NPK+ compost (+NPK+COMP)	T16		NPK+ compost (+NPK+COMP)

The dry matter yield was gathered after harvesting the plants from each pot. The plants were harvested with the roots intact, then thoroughly washed with running water. Plant samples were air-dried in the laboratory for 48 hrs. The shoots, roots and kernels were separated, and oven-dried for 48hrs at 60⁰C, then plant samples were weighed for the shoot and root yield; and the total dry yield and the shoot: roots ratios were calculated. Plant height for corn was recorded during harvest.

3.6. Planting and Activity Calendar

The planting calendar indicates that each crop was harvested after 18 weeks of maturity. Soil samples were collected after 4 weeks, after 8 weeks and 12 weeks respectively prior to transplanting spinach seedlings (Table 3.2). However, during the growth of rape seeds, the soil samples were collected 15 weeks after harvesting the last soil samples spinach. Corn soil samples were collected after harvesting rape plants and the last soil samples were collected during harvesting of corn plants (Figure 3.2).

Table 3.2. Planting sequence and operations conducted in the whole period of experiments.

Activity	Weeks																														
	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40	42	44	46	48	50	52	54	56	58	
1. Planting		SP									R											C									
2. Harvest									SP											R											C
3. Soil sampling	X		X				X		X											X											X
4. Amendments	X																														
5. Fertilizers	X									X											X										

SP = spinach, R= rape, C = corn

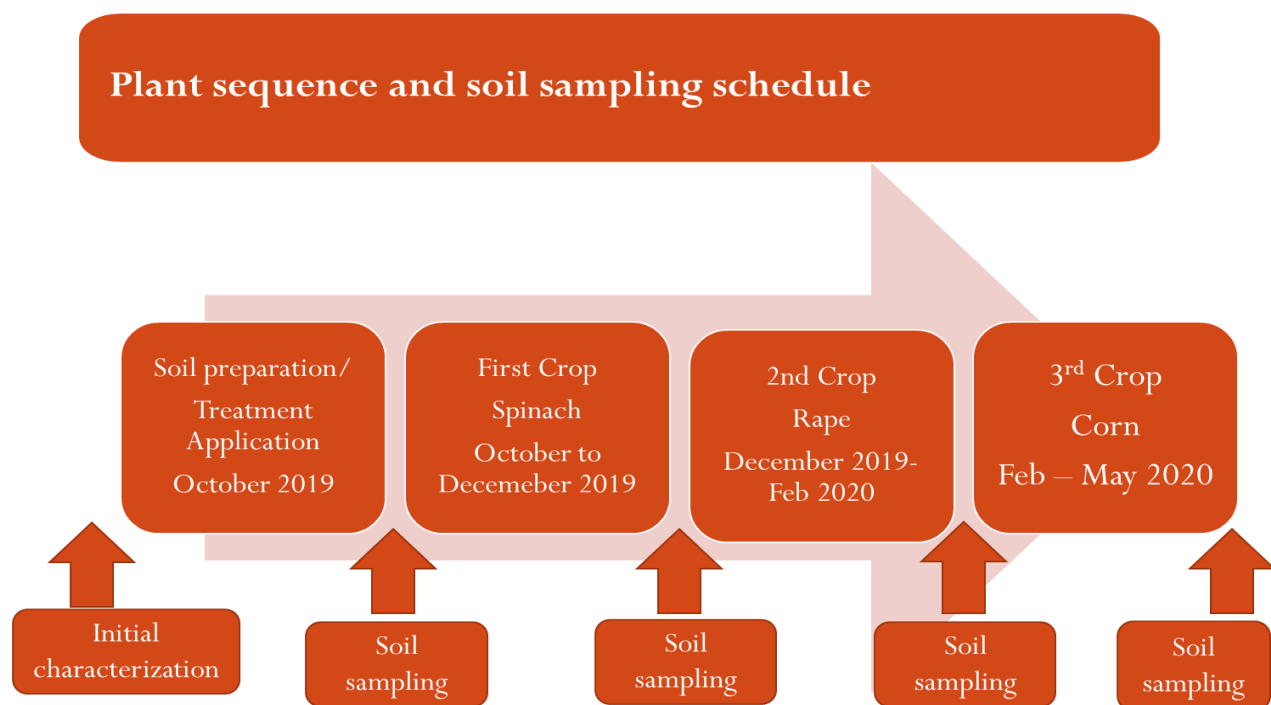


Figure 3.2. Flowchart of the planting sequence and soil sampling during the entire duration of the experiments.

Fly ash was added once off as amendment before planting spinach while fertilizers were applied before planting other crops.

3.7. Plant Tissue Analysis

The oven dried samples of spinach, rape and corn were analyzed for the heavy metal contents. Plant samples were grounded to powder using a food processor before chemical analysis. The powdered plant tissue samples were analyzed for total heavy metal contents by wet acid digestion using a Microwave digester (Ethos Easy). Approximately, 0.5g of the tissue samples were weighed into a microwave vessel tube, added with 8 ml concentrated nitric acid (HNO_3) and 2 mL of 37% hydrogen peroxide (H_2O_2), and digested for 2hrs at 200°C . The volume of the digest was adjusted to 25 mL then filtered using Whatman's No 42-filter paper. The concentration of As,

Cr, Cu, Mn, Ni, Pb, and Zn were analyzed using ICP OES (Thermo Scientific, iCAP 7000 Series). All analyses were performed in duplicates to ascertain accuracy.

3.8. Soil Sampling and Analysis

Soil samples were collected periodically from each pot using a core sampler (5 cm diameter x 8 cm height) during the 4th and 8th weeks after planting (WAP) of spinach; and 12th WAP (3rd week after planting of rape). The soil samples were air-dried, sieved to remove debris and large roots before chemical analysis. The pH and EC of the soil collected on the 4 WAP, 8 WAP, and 12 WAP were determined using a portable pH/EC meter at a ratio of 1:2 by distilled water after shaking for 2hrs. The total heavy metals contents were analyzed for soil samples collected on the 4th WAP by acid digestion of approximately 0.3 g samples treated with 8 ml concentrated HNO₃, 1 mL concentrated hydrochloric acid (HCl), and 1 mL concentrated hydrofluoric acid (HF) in a microwave digester at 200°C for 1 hour. After digestion of soil samples, the volume of the digest was adjusted to 25 mL and filtered using Whatman No 42. The available fraction of heavy metals in soil was determined on samples collected on the 8th WAP using 0.01 M calcium chloride solution (1:2, soil: CaCl₂ solution) after shaking for 1 hour and filtered using Whatman filter paper No 42. The concentration of the heavy metals from digest and extracts was quantified using ICP-OES. For all the chemical analyses, samples were analyzed in duplicates and an internal standard with known concentration was included as a reference check. When the values have more than 10% variation, the samples are reanalyzed.

3.9. Statistical Analysis

A two-factorial ANOVA in CRD was used to analyze the data for each type of soil and crop. After observing significant differences, Turkey`s test was performed for treatment mean at a 5% level of significance. Each parameter was analyzed separately per cropping season.

Chapter 4

Results and Discussion

4.1. Elemental composition of Morupule Fly Ash

Morupule fly ash is alkaline in nature with a pH value of 8.28, electrical conductivity of 2300 mS/m and low organic matter content (0.01%) due high combustion temperature in the furnace (see Tables 4.0 and 4.1). The high EC in fly ash compliments the low EC of the representative soils which improve the nutrients availability for plant uptake. Morupule fly ash contains both essential and non-essential elements. Essential elements include Zn (32 mg kg⁻¹), Cu (23 mg kg⁻¹), Mn (796 mg kg⁻¹), Fe (36 222 mg kg⁻¹), S (16 405 mg kg⁻¹), Ca (119 230 mg kg⁻¹), Mg (ND), Cl (232 mg kg⁻¹) and Ni (66 mg kg⁻¹), non-essential elements include As (11 mg kg⁻¹), Hg (8.6 mg kg⁻¹), Ba (614 mg kg⁻¹), Rb (17.8 mg kg⁻¹), V (206 mg kg⁻¹), Cr (159 mg kg⁻¹), Sr (535 mg kg⁻¹), Zr (374 mg kg⁻¹) and Pb (51 mg kg⁻¹). However, fly ash does not contain nitrogen because of high combustion temperature during processing. Table 4 presents the trace elements in Morupule fly ash which agrees with elemental composition of Australian Coal Fly Ash (Tauanov et al., 2020). The results obtained in the study corroborates findings in this study were application of higher rates of fly ash reduced the growth of the series of crops planted in two representative soils.

4.2 Liming potential of fly ash

The calcium carbonate equivalent of the Morupule fly ash was about 98% based on several test done using back titration method. Similarly, Figure 4.1 shows the changes of soil pH and

Table 4.0. Chemical properties of soils, fly ash and compost used in the experiment.

Properties	Selebi Phikwe soil	Tswapong soil	Fly Ash	Compost	
pH	5.03	7.60	8.8	7.6	
Electrical Conductivity (mS/m)	144	83	2370	890	
% Organic Matter	3.06	3.89	0.012	42.28	
% Total N	0.58	1.12	0.00	10.87	
Particle Size Distribution					
%Sand	65.92	60.39	21.05		
%Silt	31.29	39.61	45.25		
%Clay	2.79	1.96	33.7		
Total Concentration of Essential Elements for Plants (mg/kg)	Soil		Fly Ash	Compost	Critical Limits for Soils
Phosphorus	ND		938	40,000	
Potassium	8639.67	9642.67	1676	60,000	
Sulfur	586.00	559.50	34472	ND	
Calcium	8271.64	6596.67	16614	ND	
Iron	17,146.67	15,109.67	6	ND	
Cu	206.00	76.506	36322		
Mn	461.00	242.68	63.20	38.27	100-150
Ni	153.50	153.50	396.71	432.48	400
Zn	43.60	22.04	78.25	5.17	25-50
			25.31	426.48	150-500
Total Concentration of Other Non-Essential Elements for Plants	Soil	Soil	Fly Ash	Compost	Critical Limits for Soils
As	2.00	2.32	10.08	ND	20
Cr	384.00	216.20	159.26	ND	150
Pb	16.33	39.25	119.33	2.18	90

determine the amount of FA needed to raise the pH of the soil by incubation method. The pH of the soil increased after 4 weeks and fluctuated slightly during the 90 days incubation period. The electrical conductivity of the soil rose abruptly during the first 30 days of incubation and decline slightly prior to stabilization at 60 days after the onset of incubation.

Table 4.1. Elemental Composition of Morupule Fly Ash

Essential Elements	Concentration (mg/kg)	Non- essential Elements	Concentration (mg/kg)
Zn	32	As	11
Cu	23	Hg	8.6
Mn	796	Ba	614
Fe	36222	Rb	17.8
S	16 405	V	206
Ca	119 230	Cr	159
Mg	ND	Sr	535
Mo	ND	Zr	374
Cl	232	Pb	51
Ni	66		
P	ND		

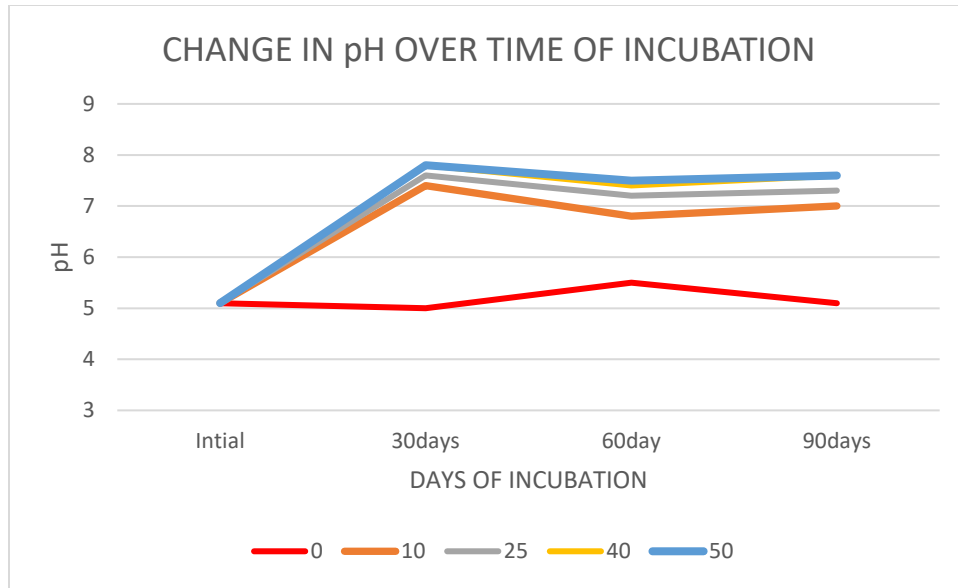
ND= Not detected

Based on the pH data on the 60th day, the amount of FA required to raise the pH of Selebi-Phikwe soils could be estimated using the polynomial equation in Figure 4.2. The high alkalinity of Morupule fly ash is responsible for the increase in the soil pH and this could be attributed to high MgO and CaO contents (Gitari et al., 2010), and the fast release of basic cations such as Ca, Mg, and Na, and the OH ions from the mineral contents (Tejasvi and Kumar, 2012). Similarly, this high mineral contents contribute to increase soil EC.

4.3. Effect of Fly Ash Amendments and Nutrient Sources on the Growth, Yield and Quality of Spinach, Rape and Corn in Tswapong Soil and Selebi-Phikwe Soil

4.3.1. Yield of Spinach, Rape and Corn in Tswapong Soils

The dry matter yield of spinach grown in Tswapong agricultural soils with different rates of fly ash amendments and nutrient sources harvested 40 days after planting was presented in Table 4.2. There was a highly significant interaction effect of FA on the shoots and total dry weight of



Rates of FA

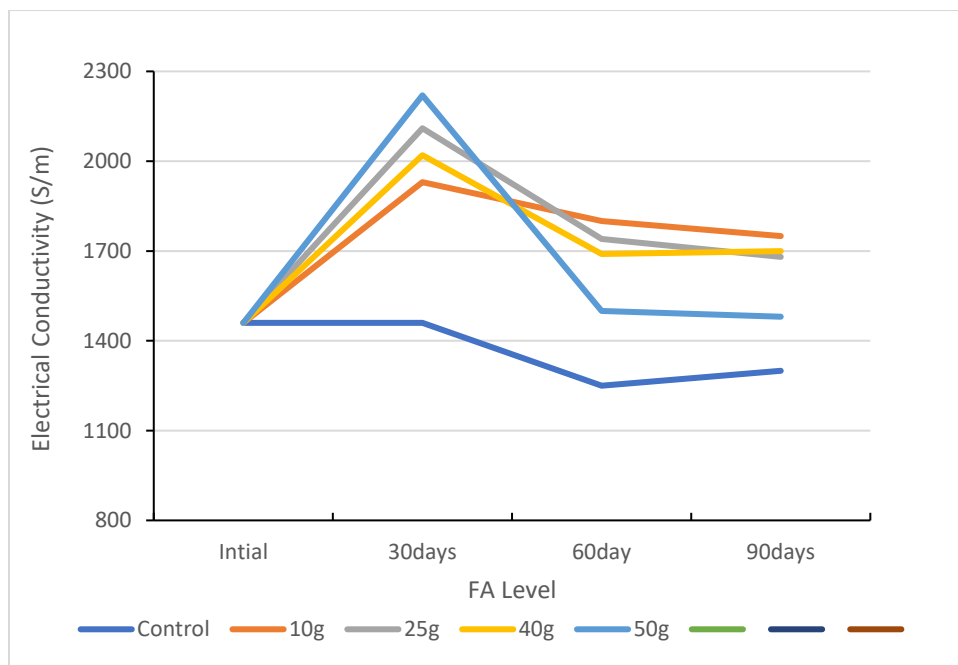


Figure 4.1. Changes of pH and EC of Selebi-Phikwe soils amended with different rates of fly ash incubated for 90 days.

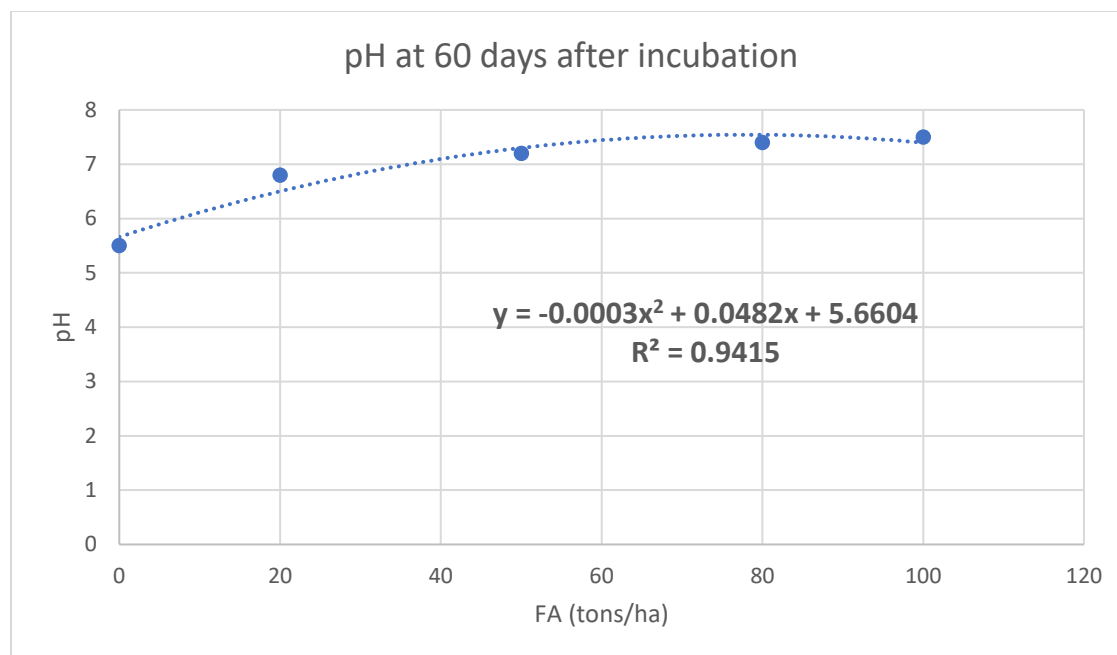


Figure 4.2. Scatter diagram between the pH and the amount of Fa applied to soil to raise a particular pH level.

spinach while the main effect of FA was observed in roots and the shoot/root ratio. Specifically, the highest shoots and total dry weights were observed in treatments with 10% FA+NPK+Compost which is statistically similar to 10% FA+ compost and 15% FA+ NPK. The enhanced dry yield is due to the availability of essential nutrients such P, K, S, Ca, Fe, Cu, Mn, Ni and Zn except for nitrogen from fly ash. Moreover, this is due to addition of fertilizers which provide the readily available nutrients to plants. On the other hand, the application of fly ash at 5% FA with or without additional nutrients did not result in a significant increase in shoots and total dry matter yield as compared to the control (0%FA -No fertilizer) but significantly increased the root dry weight. This would indicate that nutrient added into the soil from 5%FA is not high enough to facilitate an optimum growth of shoots while the significant increase of root growth could be due to reduction

of bulk density (Tejasvi and Kumar, 2012.). Similarly, the 15% FA had significantly increased the root dry weight as compared to the control by 36% across the different nutrients added.

For the second crop, the yield of rape was significantly affected by the interaction of FA and nutrient sources (see Table 4.3). Significantly high shoot, root, and total yield were obtained in treatments with 10% FA+NPK+Compost and 10% FA+NPK. All plants grown in soil with FA amendments had higher dry matter yield compared to the control and it appeared that in treatments with 5% FA, with different nutrient sources have comparable dry matter yield from each other but their yield is significantly higher than the control. In 15% FA, the application of inorganic NPK yielded much higher compared to its counterpart. These results indicate that the observed effect of fly ash on the first crop was sustained for the subsequent cropping. The shoot/root ratio in 5% FA and 10% FA were higher than those with 0% FA and 15% FA regardless of the added nutrients and this indicate that at FA rates between 5-10%, it favors shoot growth and development.

Table 4.4 shows corn grown in Tswapong soils with different rates of fly ash amendments and nutrient sources harvested 40 days after planting. There is a highly significant interaction effect of FA application and nutrient sources on all the growth parameters. Specifically, the addition of 5% FA+ combination of nutrient sources resulted in the highest dry weight of shoots and total dry yield among treatments, while addition at 10% FA+ combination of nutrient sources resulted in the highest dry weight of roots and grain. In 5%FA+NPK+Comp, the shoots observed an increase of 5.27 times more than the control while the grain observed an increase of 11.3 times comparable to the control. Based on the control, the total dry weight observed an increase of 5.10 times more than the control due to addition of 10%FA. The shoot/root ratio of plants from 10% FA+ combination of nutrient sources and 15%FA+ compost was significantly higher compared to 5%FA alone and 5% FA+ compost. An increase in the dry yield matter at 10%

Table 4.2. Dry matter yield and the shoot/root ratio of spinach grown in Tswapong soils as affected by fly ash and nutrient sources¹.

Treatment Combination		DMY of Spinach (g plant ⁻¹)			Shoot/Root Ratio
FA Level	Fertilizer	Shoot	Roots	Total	
0%FA	-NF	1.99c	1.53d	3.52c	1.30b
	+COMP	2.29bc	1.57d	3.86c	1.46b
	+NPK	2.64abc	1.61d	4.25bc	1.64b
	+NPK+COMP	2.54ab	1.62d	4.16bc	1.57b
5%FA	-NF	2.36ab	1.65c	4.01c	1.43b
	+COMP	2.51ab	1.67c	4.18c	1.50b
	+NPK	2.39ab	1.68c	4.07c	1.42b
	+NPK+COMP	2.38ab	1.73c	4.11c	1.38b
10%FA	-NF	2.77abc	1.76b	4.59bc	1.61a
	+COMP	3.67ab	1.77b	5.47ab	2.09a
	+NPK	2.99abc	1.83b	4.82bc	1.63a
	+NPK+COMP	4.07a	1.91b	6.26a	2.28a
15%FA	-NF	2.65abc	1.97a	4.39c	1.23b
	+COMP	2.60abc	2.1a	4.72bc	1.25b
	+NPK	3.49abc	2.25a	5.74abc	1.55b
	+NPK+COMP	2.44ab	2.30a	4.74c	1.06b
p values					
FA		0.000***	0.020**	0.000***	0.025**
Fertilizer		0.150NS	0.254NS	0.031**	0.301NS
FA x Fertilizer		0.070**	0.927NS	0.006**	0.100NS
Reference Values		0.30 mg/kg	2.3 -mg/kg	70mg/kg	30-500 mg/kg

¹ Means within a column followed by the same letter(s) are not significantly different from each other based on Tukey's test at 5% level of significance. *=significant, **=highly significant, ***= very highly significant; NS = non-significant

application rate of fly ash could be due to the ability of fly ash to improve the structure and enhance nutrient availability whereas at the 15% application rate the excess essential nutrients were now toxic hence the high root yield as a defense mechanism. A similar study was conducted by Sharm and Kalra, 2006, which found that the application rate of fly ash at 10ton/ hectare improved soil structure and nutrient availability which leading to a high yield.

Overall, the application of fly ash to Tswapong soil increased the dry matter the yield of crops. The application of 10% FA increased the dry matter yield of spinach and rape, while corn

obtained the optimum yield with 5% FA application. This indicate that 10% FA is overall optimum rate of FA application. Morupule fly ash contains essential elements such as P, K, S, Ca, Fe, Cu, Mn, Ni and Zn needed for plant growth that can be sourced from soil, except nitrogen (see Table 4.0).

These nutrients can help improve the plant's growth and development as shown by several studies on rice (Panda et al., 2019; Yu et al., 2019), pumpkin crop (Ahmad et al., 2021), wheat (Kausar, 2007), chickpea (Khan and Saboor, 2012), and potato (Tomar and Khan, 2015). Like in these studies, the results from this study indicate improvement of growth and dry matter yield due to FA amendment and can be attributed to an increase in concentrations of most essential elements which are beneficial at certain levels for utilization of a specific plant species (see Table 4.0). A study conducted using 25% fly ash improved the growth of rice seedlings and up to 30% by weight for pumpkin, however, the results from this study shows that for Tswapong soil, the application of fly ash beyond 10% is detrimental to plant growth and yield for all the series of crops (Table 4.2, 4.3 and 4.4).

4.3.2. Yield of Spinach, Rape and Corn in Selebi Phikwe soil

Table 4.5 presents the dry matter yield of spinach grown in Selebi-Phikwe agricultural soils with different rates of fly ash amendments and nutrient sources harvested 40 days after planting. There was a high significant interaction effect of FA and nutrient source on the dry matter yield of spinach. Specifically, the highest shoots, root, and total dry matter yield were obtained in treatment

Table 4.3. Dry matter yield and the shoot/root ratio of rape grown in Tswapong soils as affected by fly ash and nutrient sources¹.

Treatment Combination		DMY of Rape (g plant ⁻¹)			Shoot/Root Ratio
FA Level	Fertilizer	Shoot	Roots	Total	
0%FA	-NF	3.12fg	1.49d	4.61f	2.10ab
	+COMP	2.95g	1.54cd	4.51f	1.92ab
	+NPK	4.5cdef	1.56cd	6.06cdef	2.88ab
	+NPK+COMP	4.06defg	1.62bcd	5.68ef	2.51ab
5%FA	-NF	5.20bcdef	1.81bcd	7.01def	2.87a
	+COMP	5.70bcd	1.85bcd	7.55cde	3.08a
	+NPK	5.33bcde	1.89bcd	7.22cde	2.82a
	+NPK+COMP	5.75bcd	2.01bcd	7.76cde	2.86a
10%FA	-NF	5.67bcd	2.16bcd	7.83cde	2.63a
	+COMP	5.96bcd	2.19bcd	8.15cd	2.72a
	+NPK	7.28ab	2.28bcd	9.56ab	3.19a
	+NPK+COMP	8.09a	2.3abcd	10.39a	3.52a
15%FA	-NF	3.51efg	2.36abcd	5.87f	1.49b
	+COMP	4.25defg	2.56abc	6.81def	1.66b
	+NPK	6.42abc	2.67ab	9.09bc	2.40b
	+NPK+COMP	3.06g	3.34a	6.40f	0.92b
p values					
FA		0.000***	0.000***	0.000***	0.005**
Fertilizer		0.000***	0.012**	0.000***	0.416NS
FA x Fertilizer		0.000***	0.040*	0.000***	0.180NS

¹ Means within a column followed by the same letter(s) are not significantly different from each other based on Tukey's test at 5% level of significance. *=significant, **=highly significant, ***= very highly significant; NS = non-significant

with 5%FA+Comp while all other treatments are higher than the control. The highest roots and the shoots/ roots ratio were obtained in treatments with 15%FA+Comp. The application of fly ash at 5% and 15% also increased the shoot dry weight 19-26% and 23-75% based on the control (0%FA-no fertilizer), respectively, regardless of the nutrient sources. The increase in total dry matter yields due to FA application ranged from 13% to as high 86% based on the control.

This result indicates the potential of Morupule fly ash to improve the yield of crops in an acidic soil with elevated levels of heavy metals. Similar to the results obtained in Tswapong soils,

Table 4.4. Dry matter yield and the shoot/root ratio of corn grown in Tswapong soils as affected by fly ash and nutrient sources¹.

Treatment Combination		Dry Matter Yield of Corn (g/plant)				
FA Level	Fertilizer	Shoots	Roots	Grain	Total	Shoot/Root Ratio
0% FA	-NF	6.60c	1.16b	0.023c	7.79c	3.91b
	+COMP	5.48c	1.34b	1.66c	8.48c	4.43b
	+NPK	14.60c	2.86b	5.22c	22.68b	5.27b
	+NPK+COMP	24.94b	4.89b	9.31b	39.13a	5.19b
5% FA	-NF	7.95c	1.46b	3.03c	12.45c	5.69b
	+COMP	12.34c	2.02b	0.00c	14.36c	6.15b
	+NPK	17.39b	3.83b	9.39a	30.60b	4.68b
	+NPK+COMP	32.61a	8.12a	7.22b	47.95a	4.26b
10%FA	-NF	12.86c	1.37b	0.92c	15.14c	9.34a
	+COMP	12.99c	1.41b	5.55c	19.95b	9.25a
	+NPK	18.85b	4.71b	0.00c	23.56b	3.99b
	+NPK+COMP	22.60b	8.69a	11.08a	42.37a	2.63b
15% FA	-NF	4.99c	1.01b	0.41c	6.40c	5.31b
	+COMP	1.98c	1.17b	0.00c	3.15c	2.11b
	+NPK	17.13b	2.73b	6.39c	26.24b	6.30b
	+NPK+COMP	17.34b	3.03b	10.21a	30.57b	4.03b
p values						
FA		0.000***	0.000***	0.000***	0.000***	0.009***
Fertilizer		0.000***	0.000***	0.000***	0.000***	0.096**
FA x Fertilizer		0.000***	0.000***	0.000***	0.000***	0.004***

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. *-significant; ** highly significant; *** very highly significant; NS-non-significant.

FA amendment increased yield but the maximum yield for spinach was obtained at lower FA rate at 5%. This indicate that for Selebi-Phikwe soils with elevated levels of heavy metals, higher rates of FA could be detrimental to crop growth and development which could be due to additional heavy metal loadings in soil. Additional growth improvement due to compost application affirmed the benefits that compost can provide on reducing availability of heavy metals in soils aside from the myriads benefits it provides on plant growth (Ultra., 2020a; Ultra., 2020b). Belyaeva and Haynes, 2012, demonstrated that FA combined with organic amendments improved the growth

Table 4.5. Dry matter yield and the shoot/root ratio of spinach grown in Selebi-Phikwe soils as affected by fly ash and nutrient sources¹.

Treatment Combination		Dry Matter Yield of Spinach (g/plant)			
FA Level	Fertilizer	Shoot	Roots	Total	Shoot/Root Ratio
0%FA	-NF	1.67c	1.40c	3.08c	1.19b
	+COMP	3.02bc	2.19b	5.21b	1.34b
	+NPK	2.66bc	1.97b	4.63b	1.24b
	+NPK+COMP	2.69bc	1.75b	4.44b	1.47b
5%FA	-NF	3.60abc	2.23b	5.83b	1.59ab
	+COMP	7.52a	4.90a	12.42a	1.56ab
	+NPK	5.04abc	2.88ab	7.93ab	1.73ab
	+NPK+COMP	4.25abc	2.66b	6.91ab	1.6ab
10%FA	-NF	5.10abc	3.04ab	8.14ab	1.67ab
	+COMP	6.24ab	2.82ab	9.06ab	2.23ab
	+NPK	5.67abc	2.56b	8.23ab	2.44ab
	+NPK+COMP	6.01ab	3.13ab	9.1ab	1.93ab
15%FA	-NF	3.53abc	1.93b	5.46b	1.89ab
	+COMP	5.74abc	1.85b	7.60ab	3.81a
	+NPK	4.39abc	2.67b	7.06ab	1.63ab
	+NPK+COMP	5.07abc	2.56b	7.63ab	1.97ab
p values					
FA		0.000***	0.020**	0.000***	0.025**
Fertilizer		0.150NS	0.254NS	0.031**	0.301NS
FA x Fertilizer		0.070**	0.049*	0.006**	0.031*

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. *-significant; ** highly significant; *** very highly significant; NS-non-significant.

Rhodes grass which was attributed to enhanced availability of nutrient such N, P, K, and Mg, increased the CEC, and improvement of microbial activity.

The dry yield of rape was significantly affected by the interaction of FA and nutrient sources (see Table 4.6). Significantly higher shoot, root and total yield was obtained in most treatments applied with FA as compared to the control and the treatments that have the highest yield recorded in 5%FA+NPK amounting to 11.37 g/plant in total dry matter yield.

Table 4.6. Dry matter yield and the shoot/root ratio of rape grown in Selebi-Phikwe soils as affected by fly ash and nutrient sources¹.

Treatment Combination		Dry Matter Yield of Rape(g/plant)			
FA Level	Fertilizer	Shoots	Roots	Total	Shoots/ roots ratio
0%FA	-NF	0.47c	0.45d	0.92c	0.35d
	+COMP	1.0c	0.92cd	1.92c	0.73cd
	+NPK	1.06c	0.89cd	1.95c	1.22bcd
	+NPK+COMP	1.55bc	1.20bcd	2.75bc	1.42bcd
5%FA	-NF	4.45abc	1.83abcd	6.28abc	2.41abc
	+COMP	6.27ab	2.18abcd	8.45ab	2.87ab
	+NPK	7.69a	3.69a	11.37a	2.26abc
	+NPK+COMP	8.09a	2.83abc	10.92a	2.79abc
10%FA	-NF	6.41ab	2.98abc	9.39a	2.15abc
	+COMP	4.52abc	1.86abcd	6.38abc	2.38abc
	+NPK	3.14abc	1.8abcd	4.95abc	1.66abcd
	+NPK+COMP	3.69abc	2.06abcd	5.76abc	1.73abcd
15%FA	-NF	3.37abc	1.62abcd	5.0abc	2.08abcd
	+COMP	4.58abc	2.01abcd	6.59abc	2.28abc
	+NPK	7.37ab	3.25ab	10.6a	2.27abc
	+NPK+COMP	7.78a	2.71abc	10.49a	3.31a
P values	FA	0.000***	0.000***	0.000***	0.001***
	Fertilizer	0.098NS	0.001***	0.000***	0.403NS
	FA x Fertilizer	0.050*	0.023*	0.001**	0.029*

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. *-significant; ** highly significant; *** very highly significant; NS-non-significant.

However, all treatments receiving FA were statistically similar to each other and the total dry matter yield ranged from 5.0 to 11.37 g/plant. Application of nutrients enhanced the dry yield of rape, but such increase was not significant when compared to the control. Similarly, all treatments with FA regardless of nutrient sources have higher shoot: root ratio as compared to those treatments without FA. This result indicates how the effect of FA on crops would change over time. It appeared that for rape as a second crop, a general improvement of growth could be obtained with FA application, but optimum yield could be at lower rates in the presence of NPK fertilizer.

This would imply that the benefits that can be derived from FA amendments can be sustained as long as essential nutrient for plant should be made available at optimum levels.

Table 4.7 presents the dry matter yield of corn grown in Selebi Phikwe agricultural soils with different rates of fly ash amendments and nutrient sources harvested 40 days after planting. There was a highly significant interaction effect of FA and nutrient sources on the all the growth parameters. Specifically, the highest shoots and total dry weight were obtained in 10%FA+NPK+Comp while the highest dry weight of the roots and grain were obtained in 5%FA+NPK+Comp. The addition of fly ash alone at 5% FA, 10% FA and 15% FA did not significantly increase the dry yield of corn as compared to the control. However, addition of fertilizer and in combination of compost significantly increase the yield across different rates of FA application. This result is similar to those reported by Sign and Sukul., (2019) on the improvement of growth of corn with combined application of 4 tons/hectare FA combined with 4 tons/hectare vermicompost. Combined application of NPK fertilizer and compost provide the readily available nutrients to plants from the NPK fertilizer and at the same time the benefits that could be derived from compost.

Considering the overall growth and yield performance of spinach, rape, and corn successively grown in Selebi-Phikwe soil, it appeared that 5% FA application would favor plant growth and development and such benefits could be enhanced by the combined application of synthetic fertilizer and compost. Increasing the FA rate to 10 to 15% will result to lower yield increment which could be attributed to nutrient imbalance and unfavorable impact on soil biochemical and physical properties especially at the onset of its application. 10% FA application, however, could be potentially favorable in the long- run as exemplified by the yield of corn. For

Table 4.7. Dry matter yield and the shoot/root ratio of corn grown in Selebi-Phikwe soils as affected by fly ash and nutrient sources¹.

Treatment Combination		Dry Matter Yield of Corn (g/plant)				Shoot/Root
FA Level	Fertilizer	Shoots	Roots	Grain	Total	Ratio
0% FA	-NF	5.08hi	0.75f	1.1cd	6.93hi	6.84ab
	+COMP	7.82g	1.20def	0.67d	10.18fg	7.04ab
	+NPK	12.49cde	2.33cdef	1.30cd	16.14e	5.80ab
	+NPK+COMP	6.70gh	1.36def	0.63d	8.82gh	5.71ab
5% FA	-NF	3.98ij	3.03bcde	0.34d	7.76hi	1.35b
	+COMP	10.12f	1.41def	0.57d	11.57f	7.34ab
	+NPK	18.65b	4.50bc	2.87c	26.02c	4.18ab
	+NPK+COMP	11.02ef	7.21a	12.41a	30.64b	1.53b
10% FA	-NF	3.28ij	0.83ef	0.09d	3.80j	3.94ab
	+COMP	2.16j	0.85ef	0d	3.02j	2.55ab
	+NPK	13.81c	2.42cdef	1.69cd	17.92de	5.79ab
	+NPK+COMP	26.79a	4.10bc	0.24d	35.35a	9.10a
15% FA	-NF	4.64i	0.67f	0.95cd	6.27i	7.12ab
	+COMP	6.72gh	0.88ef	0.6d	7.89ghi	9.00a
	+NPK	13.11cd	4.99ab	1.74cd	19.27d	2.64ab
	+NPK+COMP	11.55def	3.14bcd	10.24b	26.13c	3.85ab
p values						
FA		0.000***	0.000***	0.000***	0.00***	0.009***
Fertilizer		0.000***	0.000***	0.000***	0.000***	0.096**
FA x Fertilizer		0.000***	0.000***	0.000***	0.000***	0.004***

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. *-significant; ** highly significant; *** very highly significant; NS-non-significant.

Selebi Phikwe, the application of fly ash from 5% to 10% FA showed to improve the dry matter of spinach, rape and corn. Similarly, the presence of essential nutrients in fly ash is attributed to the increase in dry matter of the series of crops (see Table 1). The addition of 15% FA, however, reduced the dry matter due to excessive uptake of essential nutrients. Application of FA at high rates could also cause a nutrient imbalance that may disrupt the physiological process such as the reduction in photosynthetic pigments due to low availability of N and P, and high availability of heavy metals (Shakeel et al., 2019; Varshney et al., 2019).

The addition of nutrients gave a superior yield in the first crop (spinach) but for the second (rape) and last crop (corn), the combination of inorganic NPK and compost have the best yield. At 0% to 10%, fertilizer application supplied the nutrients needed for plant use while maintaining favorable EC but at 15% FA, the additional inorganic NPK will contribute to existing high EC beyond the optimal EC levels in the soil. Compost could reduce the availability of excessive essential and non-essential elements from fly ash that may be detrimental to plant growth by providing an additional adsorption matrix in soil.

4.4. Heavy Metal Concentration in Plant Tissues of Spinach, Rape and Corn grown in Tswapong and Selebi-Phikwe soils as Affected by Fly Ash amendments and Nutrient Sources

4.4.1. Heavy metal concentrations in plant tissues harvested from Tswapong soils

4.4.1.1 Heavy metal concentration in the tissues of spinach grown in Tswapong soils

Heavy metal concentration in shoots of spinach

Except for As, the heavy metal concentration in shoots of spinach grown in Tswapong soil was affected by the interaction of the different rates of fly ash amendment and nutrient sources (see Table 4.8). The concentration of As ranged from 0.00 to 0.24 mg kg⁻¹ and in treatments 5%FA-NF, 5%FA-NPK, and 10%FA-NF are below the detection limit. In the absence of additional nutrients, the concentration of Cr in shoots was reduced by 5% FA and 15% FA but increased by 10% FA in which a concentration of Cr equivalent to 10.49 mg kg⁻¹ was observed. In 0% FA, the control had 7.08 mg kg⁻¹ Cr in shoots, and this was significantly reduced by the presence of compost, NPK, and its combination. The addition of combined compost+ NPK at 5%FA increased

Table 4.8. Heavy metal concentration in the shoots of spinach (*Spinacia oleracea* L) grown in Tswapong soil as affected by fly ash amendment and nutrient sources.¹

Treatment combination		Heavy Metal Concentrations (mg kg-1)						
FA	Fertilizer	As	Cr	Cu	Mn	Ni	Pb	Zn
0%FA	-NF	0.24a	7.80b	5.79ef	68.43b	2.51a	0.50b	22.27b
	+COMP	0.04a	2.23fgh	7.79de	30.57f	0.82fg	0.24b	20.63bcd
	+NPK	0.12a	0.47h	7.10de	60.38d	0.25h	0.11b	21.19b
	+NPK+COMP	0.12a	1.04gh	5.69ef	36.77e	0.33h	0.26b	17.90e
5%FA	-NF	0.00a	5.32cd	5.74ef	66.53b	0.97ef	0.163b	22.27b
	+COMP	0.05a	3.94def	11.62b	36.27e	1.33c	2.02a	8.91gh
	+NPK	0.00a	4.66de	14.14a	63.95bc	0.73g	0.33b	10.94g
	+NPK+COMP	0.02a	6.67bc	9.80c	32.91f	2.49a	0.28b	18.95cde
10%FA	-NF	0.00a	10.49a	6.87def	68.49b	1.96b	0.5b	27.17a
	+COMP	0.07a	3.39def	7.68de	38.71e	1.24cd	2.23a	18.54de
	+NPK	0.02a	0.68gh	6.02ef	73.09a	0.12h	0.36b	21.51b
	+NPK+COMP	0.12a	0.72gh	8.29cd	32.28f	0.24h	0.38b	16.80ef
15%FA	-NF	0.04a	1.20gh	6.37def	62.70bcd	1.08de	0.42b	14.79f
	+COMP	0.03a	3.21ef	7.39de	75.19a	6.61g	0.28b	22.17b
	+NPK	0.03a	2.73efg	4.76f	4.85g	2.44h	0.39b	5.94i
	+NPK+COMP	0.15a	6.67bc	5.94ef	6.67g	0.68g	0.36b	6.91hi
P values	FA	0.287N	0.000***	0.000***	0.000***	0.000***	0.003**	0.000***
		S						
	Fertilizer	0.203N	0.000***	0.000***	0.000***	0.000***	0.019NS	0.000***
		S						
FAx Fertilizer		0.721N	0.000***	0.000***	0.000***	0.000***	0.000***	0.000***
		S						
Maximum allowable levels in vegetables (mg kg ⁻¹ , d.w.)		0.30 ²	2.3 ³	40 ³	30-500 ³	5.0 ³	0.30-0.50 ³	60 ³

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. *-significant; *** very highly significant; NS-non-significant.

-NF = no fertilizer; +COMP=compost; +NPK = with inorganic NPK; +NPK+COMP = combine NPK and compost

²Yanez et al. 2019

³Latif et al. 2018

the Cr concentration when compared to 5%FA-NF but such increase was only comparable to 0FA-NF (control). Treatments 10%FA+NPK and 10%FA+NPK+compost resulted in a lower Cr concentration compared to 10%FA+compost. In 15%FA treatments, the Cr concentration followed this order combination> compost> inorganic NPK> control respectively.

Without the nutrient addition, the shoot-Cu did not differ significantly with different rates of FA application. Similarly, in 0%FA and 15%FA treatments, there were no significant differences due to nutrients sources but in 5%FA, Shoot-Cu was significantly increased due to the nutrient addition wherein 5%FA+NPK had the highest increment followed by 5%FA+compost and 5%FA+NPK+compost. In 10%FA treatments, only the 10%FA+NPK+compost had significantly higher shoot-Cu as compared to other treatments of the same FA level as well as the control (0%FA-NF).

For shoot-Mn, different rates of FA without nutrients addition did not significantly vary the concentration which ranged from 62.70 to 68.49 mg kg⁻¹. In 0%FA and 5%FA, all nutrient addition had significantly reduced the shoot-Mn in which compost and combination of NPK+compost have a higher magnitude of reduction than the NPK treatment. In 10%FA, compost and combination of NPK and compost significantly reduced while NPK had significantly increased the shoot-Mn. Whereas in 15%FA, compost significantly increased while NPK and combination of NPK+compost reduced the shoot-Mn.

Application of FA alone at different rates significantly reduced the shoot-Ni from 2.51 mg kg⁻¹ in the control (0FA-NF) to 0.98 mg kg⁻¹ in 5%FA-NF, 1.96 mg kg⁻¹ in 10%FA-NF, and 1.08 mg kg⁻¹ in 15%FA-NF. Except for 5%FA+NPK+compost, all other treatment combinations have significantly lower shoot-Ni compared to the control. The degree of reduction in the Ni concentration was more pronounced in treatments with NPK than in those with compost. The concentration of Pb in the shoots from different treatments are statistically similar except those treatments with 10%FA+compost and 5%FA+compost. The shoot-Zn concentration was reduced due to 15%FA application but increased by 10%FA in the absence of nutrient sources while 0%FA and 5%FA have comparable values. Reduction to more than 50% than the concentration of the

control was recorded in 15%FA+NPK, 15%FA+NPK+compost, and 5%FA+compost. Other treatments have also lower values than the control but of narrow difference.

The shoots of spinach grown on this soil without FA and fertilizers has As, Cu, Mn, Ni, Pb, and Zn levels below the maximum acceptable level (MAL) for vegetables. Only the concentrations of Cr and Ni have concentrations above the MAL in spinach and this could be attributed to the inherently high concentration in soil (Table 1). FA addition at 5% reduced the concentration of these metals in the shoots of spinach and the presence of fertilizer source had either increased or decreased these metals. In spinach, only the concentration of Cr is above the MAL for vegetables which could be attributed to high Cr in soils and considered to be mobile in soils and taken up easily by plants. At 10% FA, the treatments 10%FA+NPK and 10%FA+NPK+Compost has all the metal concentrations in spinach below the MAL while at 15%FA, without the fertilizer, the As, Cr, Cu Mn and Zn in spinach were below the MAL but the Ni and Pb were above the MAL. Fertilizer application in 15% FA resulted in Cr and Ni concentrations above the MAL for spinach. A general decrease of metals uptake was observed in plants that have high biomass yield. Such decrease could either be due to the dilution effect brought about by enhancing growth and biomass yield or reduction of availability due to an increase in pH and the presence of compost.

Heavy metal concentration in roots of spinach

The heavy metal concentration in the roots of spinach grown in Tswapong soil is affected by the interaction effect of fly ash and nutrient sources except for Pb (see Table 4.9). For the root-As content, 15%FA+compost had a significantly higher concentration compared to the control, but most of the treatments were below the detection limit. For root Cr, all treatments had a

Table 4.9. Heavy metal concentration in the roots of Spinach (*Spinacia oleracea* L) grown Tswapong soil as affected by fly ash amendment and nutrient sources.¹

Treatment Combination		Heavy Metal Concentration (mg kg ⁻¹)						
FA	Fertilizer	As	Cr	Cu	Mn	Ni	Pb	Zn
0%FA	-NF	0.00b	12.58a	15.37b	87.32a	8.95c	0.81a	12.07bc
	+COMP	0.17ab	6.79d	8.12de	57.23b	4.98ef	0.61a	9.45efg
	+NPK	0.03b	8.71b	14.98b	26.05i	7.28cd	0.86a	15.43bc
	+NPK+COMP	0.04ab	5.47cd	20.68a	55.05c	10.98b	0.77a	10.53def
5%FA	-NF	0.007b	1.56fg	15.93b	43.49f	6.14de	0.57a	11.58cde
	+COMP	0.01b	1.89fg	11.92c	47.50e	4.91ef	0.47a	8.53fgh
	+NPK	0.057ab	1.33g	8.35de	52.00d	2.13gh	0.43a	8.21gh
	+NPK+COMP	0.07ab	4.36de	6.27e	17.24lm	6.38de	0.42a	7.06hi
10%FA	-NF	0.11ab	3.77def	7.17e	16.58m	6.62de	0.28a	5.55i
	+COMP	0.04ab	2.83efg	14.15b	23.95j	14.02a	0.57a	5.12i
	+NPK	0.04ab	3.61def	8.28de	19.12kl	13.20a	0.50a	2.72j
	+NPK+COMP	0.037ab	2.68efg	8.12de	21.05k	6.88de	0.85a	13.30bc
15%FA	-NF	0.00b	2.33efg	6.92e	47.33e	3.20fgh	0.33a	12.53bc
	+COMP	0.44a	2.31efg	9.48d	12.32n	1.40h	0.39a	12.75bc
	+NPK	0.20ab	1.67fg	6.63e	40.03g	4.01fg	0.34a	13.52bc
	+NPK+COMP	0.14ab	4.31de	7.19e	37.37h	13.86a	0.25a	17.39a
P-values	FA	0.097NS	0.000***	0.000***	0.000***	0.000***	0.553 NS	0.000***
	Fertilizer	0.397NS	0.000***	0.000***	0.000***	0.000***	0.390 NS	0.000***
	FAxFertilizer	0.050*	0.000***	0.000***	0.000***	0.000***	0.088 NS	0.000***

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. *-significant; *** very highly significant; NS-non-significant.

-NF = no fertilizer; +COMP=compost; +NPK = with inorganic NPK; +NPK+COMP = combine NPK and compost

²Yanez et al. 2019

³Latif et al. 2018

significantly than the control with a reduction in concentration were about 30 to 89% based on 0%FA-NF. Without the nutrient amendments, the concentration of root-Cu significantly reduced due to FA addition at 10%FA and 15%FA, based on the 0%FA-NF. The addition of different nutrient sources in combination with different rates of FA resulted in reduced root-Cu except those in 10%FA+compost. The range of root-Cu concentration is 6.27 to 20.68 mg kg⁻¹. The root-Mn

concentration was significantly reduced due to FA and different nutrients as compared to the control. The lowest concentration of root-Mn was lowest in 15FA+compost which is about an 86% reduction as compared to the control. The Ni concentration in the roots was highest in 10%FA+compost, 15%FA+NPK+comopost, and 10%FA+NPK while other treatments were significantly lower than the control. On the other hand, the concentration of Pb in the roots was reduced by the application of fly ash and nutrient sources but such difference was not significant. The root-Zn was reduced in most treatments with FA and different nutrient especially in 5%FA+compost, 5%FA+NPK, 5%FA+NPK+compost, 10FA-NF, 10%FA+compost, and 10%FA+NPK. The range of Zn in the roots of spinach was between 2.72 to 17.39 mg kg⁻¹.

The concentrations of Cr, Cu, Mn, Ni, and Pb in roots are higher than spinach shoots, indicating that these metals are not easily translocated into shoots. In contrast, some treatments have lower concentrations of As and Zn in roots than in shoots indicating high translocation to above ground parts. Fly ash applications in combination with compost notably enhanced the retention of Cr and Cu in the roots which could be attributed to changes in pH that had affected the availability of these metals in the rhizosphere-root interphase. Some studies showed that sewage sludges and composts can reduce the translocation of metals to the above-ground parts (Pahura et al., 2916).

4.4.1.2. Heavy Metal Concentration in the tissues of rape grown in Tswapong soils

Heavy metal concentration in shoots of rape

Table 4.10 presents the concentration of heavy metals in the shoot of rape. Similar to the first crop, the As concentration in the shoots of Rape was not significantly affected by both factors.

Results and Discussion

The As concentration in the shoots of rape in most of the treatments was below the detection limit and the highest value obtained was 0.23 mg kg^{-1} in 5%FA+NPK. The shoot-Cr was significantly decreased by the application of different rates of FA and nutrient application by more than 70% of the concentration in the control (6.46 mg kg^{-1}). Shoot-Cu of rape was significantly higher in all treatments except for those in 10%FA+NPK. The concentration of shoot-Cu in these treatments ranged from 7.85 to 18.50 mg kg^{-1} which is more than 3 times than the control. The Mn concentration in the shoots of rape was significantly higher in all treatments as compared with control and the max shoot Mn concentration was obtained in 10%FA+composts. FA application in a combination of different nutrient sources resulted in statistically similar or lower values of Ni in the shoots with that of the control except for those in 0%FA+compost, 0%FA+NPK, 0%FA+NPK+compost, 5%FA, and 5%FA +compost. The Pb concentration in the shoots from all treatments was statistically similar to that of the control except for those in 0%FA+NPK. The concentration of Zn in the shoots of rape was significantly increased by all treatments except in 10%FA+NPK. The increase ranged from 6.26- 13.86 mg kg^{-1} and the highest Zn concentration was recorded in 15%FA+NPK+compost.

Rape grown on this soil without FA and fertilizers has As, Cu, Mn, and Zn levels below the MAL while only the concentrations of Cr, Ni, and Pb have concentrations above the MAL in rape, As indicated previously, this could be attributed to the inherently high concentration in soil (Table 4.0). At 10% FA, the treatments with or without the fertilizers have As, Cr, Cu, Mn Ni Pb, and Zn below MAL while at 15% FA, all the concentrations of metal under consideration are below the MAL except for the concentration of Ni in 15%FA-NF. Similar to Spinach, rape plants with high biomass yield have lower concentration of heavy metals which could be a dilution effect

Table 4.10. Heavy metal concentration in shoots of rape (*Brassica napus*) grown in Tswapong soil as affected by fly ash amendment and nutrient sources.¹

Treatment Combination		Heavy Metal Concentration (mg kg ⁻¹)						
FA	Fertilizer	As	Cr	Cu	Mn	Ni	Pb	Zn
0%FA	-NF	0.00a	5.35a	6.1d	14.35e	10.26ab	0.96b	8.74b
	+COMP	0.01a	0.46c	11.10c	18.71de	15.76ab	1.13b	8.37b
	+NPK	0.02a	0.72c	11.20c	25.98d	15.40ab	9.48a	6.69c
	+NPK+COMP	0.00a	0.51c	13.76b	42.98c	36.65a	0.70b	10.11b
5%FA	-NF	0.04a	0.78c	16.5b	27.73d	27.56ab	0.56b	11.81ab
	+COMP	0.21a	0.73c	18.06a	42.28c	19.57ab	0.21b	12.97ab
	+NPK	0.23a	0.52c	13.1b	46.35bc	3.98b	0.29b	10.46b
	+NPK+COMP	0.00a	0.64c	9.46c	27.30d	3.77b	0.16b	8.17b
10%FA	-NF	0.08a	0.17c	9.68c	32.74c	2.97b	0.21b	7.82b
	+COMP	0.17a	0.66c	13.15b	65.05a	3.27b	0.097b	9.89b
	+NPK	0.07a	0.01c	7.85d	36.02c	1.42b	0.097b	6.29c
	+NPK+COMP	0.00a	0.00c	15.95b	22.68d	1.67b	0.23b	13.08a
15%FA	-NF	0.013a	0.14c	16.53b	59.15b	4.93b	0.17b	11.16ab
	+COMP	0.053a	1.75b	18.50a	23.85d	3.86b	0.27b	13.38a
	+NPK	0.00a	0.16c	9.40c	29.80c	1.81b	0.18b	8.89b
	+NPK+COMP	0.00a	1.76b	14.20b	38.59bc	3.44b	0.33b	13.86a
P-values	FA	0.093NS	0.080NS	0.039NS	0.960NS	0.003**	0.283NS	0.141NS
	Fertilizer	0.105NS	0.121NS	0.227NS	0.559NS	0.565NS	0.465NS	0.167NS
	FA x Fertilizer	0.792NS	0.004**	0.389NS	0.372NS	0.005**	0.491NS	0.549NS
Maximum allowable levels in vegetables (mg kg ⁻¹ , d.w.)		0.30 ²	2.3 ³	40 ³	30-500 ³	5.0 ³	0.30-0.50 ³	60 ³

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. *-significant; *** very highly significant; NS-non-significant.

-NF = no fertilizer; +COMP=compost; +NPK = with inorganic NPK; +NPK+COMP = combine NPK and compost

²Yanez et al. 2019

³Latif et al. 2018

brought about by enhancing growth and biomass yield or reduction of availability due to an increase in pH and the presence of compost.

Heavy metal concentration in the roots of rape

The concentration of Cr, Mn, and Zn was significantly affected by the interaction of FA and nutrient sources while no significant differences in the concentration of As, Cu, Ni, and Pb in the roots of rape (see Table 4.11). Based on the control, root-Cr was significantly increased in 0%FA+compost, 10%FA+compost, and 10%FA+NPK+compost while all others have lower than the control. The root-Mn of rape was significantly higher in all treatments containing 5% and 10%FA except for 10%FA+NPK+compost while all other treatments have comparable values with control. The concentration of root-Zn was statistically similar in all treatments when compared to the control but 0FA+compost was significantly higher than 5%FA-NF, 15%FA+compost, and 15%FA+NPK.

In unamended soil, the concentration of As, Cu, Mn, Ni and Zn in the roots of rape were much higher than in the shoots. Application of fly ash increased the translocation of Cr and Ni to shoots but the application compost retained most of these elements in the roots. Similarly, the application of 5 to 10% FA enhanced Mn retention in roots of rape. It appears that the nature of the partitioning and translocation of metals differed from the type of heavy metals and varied with plant species and the chemical characteristics in the rhizosphere.

4.4.1.3. Heavy metal concentration in the tissues of corn (*Zea mays*) grown in Tswapong soil

Heavy Metal contents in the kernels of corn

Table 4.12 shows the heavy metal concentration of corn kernels as affected by fly ash. There is a highly significant interaction effect due to addition of fly ash and nutrient sources on As and Ni concentration in kernels. Specifically, the highest As concentration was observed in

Table 4.11. Heavy metal concentration in the roots of rape (*Brassica napus*) grown in Tswapong soils as affected by fly ash amendment and nutrient sources.¹

Treatment Combination		Heavy Metal Concentration (mg kg ⁻¹)						
FA	Fertilizer	As	Cr	Cu	Mn	Ni	Pb	Zn
0%FA	-NF	0.21a	3.17c	8.62d	37.41e	24.54a	0.36b	9.38abc
	+COMP	0.00a	5.55ab	10.12cd	74.55de	13.58b	0.31b	18.71a
	+NPK	0.00a	1.60d	7.02e	70.32de	5.03e	0.19b	18.30ab
	+NPK+COMP	0.05a	0.95e	7.11e	82.3de	1.28g	0.16b	12.38abc
5%FA	-NF	0.11a	1.09de	8.62d	134.47abc	1.41g	0.27b	9.12bc
	+COMP	0.073a	1.92d	10.48cd	122.75bcd	2.18f	0.32b	14.04abc
	+NPK	0.07a	1.96d	7.60e	144.95a	5.11e	0.40b	10.36abc
	+NPK+COMP	0.17a	2.85c	8.67d	114.98cd	6.81e	0.42b	12.89abc
10%FA	-NF	0.00a	2.21d	8.62d	125.02cd	5.69e	0.23b	11.8abc
	+COMP	0.06a	3.42b	9.92d	139.45ab	4.63e	0.53b	13.51abc
	+NPK	0.14a	2.16d	9.02d	106.05c	8.66d	0.33b	13.19abc
	+NPK+COMP	0.00a	6.02a	18.57b	68.11de	11.19bc	1.22a	13.17abc
15%FA	-NF	0.06a	3.0c	10.53cd	55.24de	4.61e	0.48b	9.98abc
	+COMP	0.06a	1.94d	12.65c	36.38e	3.94e	0.22b	7.20c
	+NPK	0.07a	3.01c	24.16a	62.21de	13.89b	0.64b	8.68c
	+NPK+COMP	0.00a	1.65d	11.99cd	58.60de	2.43f	0.44b	10.98abc
P-values	FA	0.172NS	0.281NS	0.026**	0.000***	0.367NS	0.138NS	0.002**
	Fertilizer	0.410NS	0.517NS	0.665NS	0.109**	0.655NS	0.415NS	0.157NS
	FA x Fertilizer	0.816NS	0.073**	0.646NS	0.003***	0.318NS	0.413NS	0.0.26**

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. *-significant; *** very highly significant; NS-non-significant.

-NF = no fertilizer; +COMP=compost; +NPK = with inorganic NPK; +NPK+COMP = combine NPK and compost

²Yanez et al. 2019

³Latif et al. 2018

treatments with 0%FA in combination with different nutrient sources, 5% FA+ NPK, 10% FA +NPK +Comp and 15%FA alone. In contrast, treatments with 15% FA+ combination of nutrient sources had concentrations beyond detection limit.

For Ni, a significantly high concentration was observed in 10%FA+NPK+Comp while treatments with concentration above the acceptable maximum allowable levels include 0%FA+NPK and 15%FA+NPK. The Cr concentration in corn kernels were statistically similar except for treatments with 0%FA+ NPK and 0%FA+NPK+Comp. The Cu concentration was highest in 10% FA+ compost while the application of 0% FA+ no fertilizer, 5% FA+ compost, 10% FA+ no fertilizer and 15% FA+ combination of nutrient sources resulted to a concentration below detection limit. Mn concentration was highest in treatments with 10% FA+ combination of nutrient sources. Addition of fly ash at 5% FA resulted in similar concentration of Mn regardless of nutrient sources. Similarly, the Pb concentration observed statistically similar concentration as the control except 0% FA+ NPK while the concentration of Zn was highest in 15% FA+ no fertilizer followed by 10% FA+ combination of nutrient sources.

Based on these results, the application of FA and different fertilizer sources resulted in increased concentration of As and Pb beyond the MAL for food products while for other metals, some treatment combinations reduced the levels under MAL. It appeared that 15% FA+ combination of nutrient sources is the only treatment that has concentration of these metals safe for human consumptions.

Heavy Metal contents in the shoots of corn

There is significant interaction effect with addition of fly ash and nutrient sources in the concentration of heavy metals in the shoots of corn at harvest (see Table 4.13). The concentration of As observed the highest concentration in 5%FA+ compost followed by 5% FA+ combination of nutrient sources. However, all other treatments observed statistically similar concentration as the control. The Cr concentration in shoots of plants from 5% FA+ combination of nutrient sources

Table 4.12. Heavy metal concentration in the grain of corn (*Zea mays*) grown in Tswapong soil as affected by fly ash amendment and nutrient sources.¹

Treatment combination		Heavy Metal Concentrations (mg kg ⁻¹)						
FA	Fertilizer	As	Cr	Cu	Mn	Ni	Pb	Zn
0%FA	-NF	0.20b	0.00b	0.00c	0.00c	0.00b	0.00b	0.00c
	+COMP	1.15a	1.72b	11.80c	10.61c	2.40b	8.94b	7.42b
	+NPK	1.11a	5.69a	11.97c	23.71b	12.15b	11.48a	13.86b
	+NPK+COMP	1.59a	5.55a	4.56c	23.63b	0.00b	9.29b	4.99b
5%FA	-NF	0.63b	3.23b	23.72b	0.75c	2.55b	5.09c	7.24b
	+COMP	-	-	-	-	-	-	-
	+NPK	1.68a	2.04b	28.97b	4.43c	0.22b	7.01b	10.82b
	+NPK+COMP	0.49b	1.73b	31.47b	0.00c	4.70b	5.76b	12.25b
10%FA	-NF	0.85b	0.00b	0.00c	6.01c	2.06b	5.78b	6.60c
	+COMP	0.74b	0.00b	50.33a	12.02c	3.99b	3.49b	11.67b
	+NPK	2.41b	0.00b	14.21c	0.00c	6.02b	3.12b	11.51b
	+NPK+COMP	1.56a	0.00b	24.63b	61.96a	34.24a	7.71b	21.49a
15%FA	-NF	1.13a	2.85b	4.99c	49.67b	6.17b	5.96b	24.13a
	+COMP	0.27b	0.00b	7.21c	46.40b	0.00b	2.47b	0.00c
	+NPK	0.62b	1.60b	15.01c	29.37b	11.90b	7.41b	4.36c
	+NPK+COMP	0.00b	0.00b	0.00c	0.00c	0.00b	0.00b	0.00c
P-values	FA	0.146NS	0.068NS	0.435NS	0.028NS	0.000***	0.095NS	0.632NS
	Fertilizer	0.417NS	0.604NS	0.137NS	0.960NS	0.083NS	0.263NS	0.967NS
	FAxFertilizer	0.001***	0.334NS	0.249NS	0.992NS	0.000***	0.056NS	0.165NS
Maximum allowable levels in vegetables (mg kg ⁻¹ , d.w.)		0.30 ²	2.3 ³	40 ³	30-500 ³	5.0 ³	0.30-0.50 ³	60 ³

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. *-significant; *** very highly significant; NS-non-significant.

-NF = no fertilizer; +COMP=compost; +NPK = with inorganic NPK; +NPK+COMP = combine NPK and compost

²Yanez et al. 2019

³Latif et al. 2018

was the highest and is statistically similar to the control. Application of fly ash in 0%FA and 5%FA observed statistically similar Cr concentration as the control while application of fly ash in 5% FA+ compost has the lowest concentration among all treatments. The concentration of Cu was

highest in 10%FA+ combination of nutrient sources while 0%FA+ NPK and combination of nutrient sources observed a concentration lower than detection limit.

The concentration of Mn was highest in 5%FA+ combination of nutrient sources and the concentration was 1.55 times more than the control. Application of 15%FA+ NPK observed the lowest concentration which was 8.45 less than the control. On other hand, the Ni concentration was highest in 5%FA+ NPK while others were statistically similar to the control. The Pb concentration observed a highest concentration in 0%FA+ NPK while all other treatments observed a statistically similar concentration to the control. For Zn, treatments with compost or in combination with synthetic NPK had significantly higher contents regardless of FA application. Hight Zn concentration was recorded in plants from 5%FA+NPK+Comp.

Table 4.14 shows a highly significant interaction effect with addition of fly ash and fertilizer source in the concentration of heavy metals in the roots of corn. Particularly, the concentration of As observed the highest concentration in 5% FA+ NPK while all other treatments observed a statistically similar concentration to the control. The Cr concentration observed the highest concentration in 0% FA+ no fertilizer while all others were statistically similar but the lowest concentration was observed in 10% FA+ compost.

Heavy Metal contents in the roots of corn

The concentration of Cu was highest in 10% FA+ combination of nutrient sources which is statistically similar to 5% FA+ combination of nutrient sources and 10% FA+ no fertilizer and NPK respectively. The concentration of Mn was highest in 0% FA+compost which was statistically similar to 0% FA+ no fertilizer. The application of fly ash at 10% FA resulted to

Table 4.13. Heavy metal concentration in the shoots of corn (*Zea mays*) grown in Tswapong soil as affected by fly ash amendment and nutrient sources.¹

Treatment combination		Heavy Metal Concentrations (mg kg ⁻¹)						
FA	Fertilizer	As	Cr	Cu	Mn	Ni	Pb	Zn
0%FA	-NF	1.32b	6.23a	13.32c	176.53b	0.00c	9.42b	11.85c
	+COMP	1.07b	5.70a	16.36c	88.28c	4.68c	9.76b	20.92b
	+NPK	1.27b	2.47ab	0.00c	100.84c	1.89c	12.83a	4.98c
	+NPK+COMP	1.26b	2.23ab	0.00c	80.46c	7.47c	7.55b	0.00c
5%FA	-NF	0.84b	5.28ab	4.91c	216.73a	4.38c	6.87b	0.00c
	+COMP	1.99a	0.14b	27.85ab	30.11c	11.80b	8.82b	18.55c
	+NPK	0.69b	6.31a	9.71c	174.82c	23.61a	10.34a	0.00c
	+NPK+COMP	1.63a	6.10a	32.73ab	274.24a	15.73b	10.06a	41.38a
10%FA	-NF	0.89b	6.64a	17.40ab	128.98a	17.43b	11.41a	11.84c
	+COMP	0.86b	4.34ab	5.45c	58.05c	16.78b	12.05a	25.19b
	+NPK	0.97b	0.00b	9.55c	63.44c	4.47c	10.05a	39.87a
	+NPK+COMP	1.59b	0.29b	50.60a	106.22a	2.47c	8.82b	0.00c
15%FA	-NF	0.67b	0.95b	5.19c	88.76c	7.85c	8.15b	4.03c
	+COMP	0.87b	0.87b	11.81c	76.07c	8.70c	7.06b	32.36ab
	+NPK	1.26b	0.76b	6.32c	20.89c	4.97c	8.10b	23.64b
	+NPK+COMP	1.01b	0.00b	7.25c	152.13b	4.76c	6.41b	0.88c
P-values	FA	0.57NS	0.001***	0.164NS	0.086NS	0.051NS	0.246NS	0.115NS
	Fertilizer	0.342NS	0.547NS	0.262NS	0.226NS	0.045**	0.24NS	0.008**
	FAxFertilizer	0.050*	0.001***	0.03***	0.026*	0.034*	0.048*	0.032*
Maximum allowable levels in vegetables (mg kg ⁻¹ , d.w.)		0.30 ²	2.3 ³	40 ³	30-500 ³	5.0 ³	0.30- 0.50 ³	60 ³

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. *-significant; *** very highly significant; NS-non-significant.

-NF = no fertilizer; +COMP=compost; +NPK = with inorganic NPK; +NPK+COMP = combine NPK and compost

²Yanez et al. 2019

³Latif et al. 2018

concentration of Mn in roots statistically similar to each other except on treatments with NPK fertilizer amendments. Similarly, the concentration of Ni was highest in 0% FA+ compost and the concentration were statistically similar to 10% FA+ compost and 5% FA+ compost nutrient sources, respectively. The application of 15% FA resulted to a no detection of Ni in roots. The concentration of Pb was highest in 0% FA+ no fertilizer while the addition of 15% FA resulted

Table 4.14. Heavy metal concentration in the roots of corn (*Zea mays*) grown in Tswapong soil as affected by fly ash amendment and nutrient sources.¹

Treatment combination		Heavy Metal Concentrations (mg kg ⁻¹)						
FA	Fertilizer	As	Cr	Cu	Mn	Ni	Pb	Zn
0%FA	-NF	4.86b	7.07a	31.6b	110.15a	6.32b	11.38a	21.03ab
	+COMP	6.11b	2.15b	18.67b	95.34ab	15.53a	10.19a	9.53b
	+NPK	9.85b	3.30ab	0.00b	110.08a	1.54b	6.95ab	10.90b
	+NPK+COMP	11.91b	0.39b	10.76b	46.07b	6.55b	7.82ab	9.35b
5%FA	-NF	10.94b	0.00b	76.31a	79.14b	3.34b	6.34ab	13.23b
	+COMP	9.92b	1.58b	0.027b	55.82b	11.40ab	11.21a	30.57a
	+NPK	46.88a	3.40ab	6.45b	46.64b	0.00b	8.32b	24.99ab
	+NPK+COMP	10.18b	2.79ab	24.22b	84.37b	2.68b	8.64b	23.97ab
10%FA	-NF	14.32b	0.58b	14.43b	107.54a	5.16b	8.71b	19.71ab
	+COMP	10.62b	4.06ab	11.81b	83.23b	9.76ab	10.06a	14.53ab
	+NPK	10.85b	0.00b	3.43b	71.73b	2.49b	6.43ab	26.35a
	+NPK+COMP	0.25b	0.00b	0.00b	0.01c	0.00b	0.063c	0.00c
15%FA	-NF	3.01b	0.00b	0.00b	0.00c	0.00b	0.007c	0.027c
	+COMP	0.2b	0.00b	0.00b	0.007c	0.00b	0.06c	0.00c
	+NPK	0.2b	0.00b	0.00b	0.013c	0.00b	0.083c	0.00c
	+NPK+COMP	0.2b	0.00b	0.00b	0.023c	0.00b	0.073c	0.00c
P-values	FA	0.042NS	0.005***	0.35NS	0.002***	0.003***	0.00***	0.001***
	Fertilizer	0.238NS	0.08NS	0.471NS	0.852NS	0.005***	0.043NS	0.675NS
	FAx Fertilizer	0.038*	0.003***	0.046*	0.047*	0.006**	0.006**	0.009**
Maximum allowable levels in vegetables (mg kg ⁻¹ , d.w.)		0.30 ²	2.3 ³	40 ³	30-500 ³	5.0 ³	0.30-0.50 ³	60 ³

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. *-significant; *** very highly significant; NS-non-significant.

-NF = no fertilizer; +COMP=compost; +NPK = with inorganic NPK; +NPK+COMP = combine NPK and compost

²Yanez et al. 2019

³Latif et al. 2018

very low concentrations regardless of fertilizer source. The concentration of Zn was highest in 5%FA+ Comp while treatments receiving 15%FA have Zn concentration beyond detection limit.

Majority of the heavy metals under consideration have higher concentration in roots followed by shoots and kernels. Application of FA at 5 to 10% tended to retain more As, Mn and

Zn in the roots as compared to other treatments. Such improved retention in roots have partially lowered the transport into shoots and kernels resulting in lower concentrations.

Tswapong soil has As, Cu, Mn, Ni, Pb, and Zn levels within the critical limits for agricultural soils while Cr is 3-fold above the suggested limit for agricultural soils by the Portuguese and Canadian regulations. Sequential cropping of spinach, rape and corn have demonstrated how FA amendments in combination with different nutrient sources have affected the uptake of metals for different crops. General observation across these different crops showed that spinach and rape have accumulated heavy metals in almost the same manner while corn showed a unique accumulation pattern. Such differences could be attributed to inherent species characteristics. Considering the overall all results, FA addition at 5% reduced the concentration of these metals in the shoots and the presence of fertilizer source had either increased or decreased these metals. At 10% FA, additional compost and fertilizer application reduced the concentrations of most metals. A general decrease of metals uptake was observed in plants that have high biomass yield and such decrease could either be due to the dilution effect brought about by enhancing growth and biomass yield or reduction of availability due to an increase in pH and presence of compost.

4.4.2. Heavy metal concentrations in plant tissues harvested from Selebi-Phikwe

4.4.2.1. Heavy Metal Concentration in the tissues of spinach grown in Selebi Phikwe

Heavy Metal contents in the shoots of Spinach

Table 4.15 presents the heavy metal concentration. There is a highly significant interaction effect between FA and nutrient sources on heavy metals contents in the shoots of spinach grown

Table 4.15. Heavy metal concentration in the shoots of Spinach grown in soils from Selebi-Phikwe as influenced by fly ash amendments and different source of fertilizer.¹

Treatment Combination		Heavy Metal Concentration in Shoots (mg kg ⁻¹)						
FA Levels	Fertilizer	As	Cr	Cu	Mn	Ni	Pb	Zn
0% FA	-NF	0.33a	1.00i	66.04a	88.37c	47.71a	0.00d	26.04a
	+COMP	0.00a	1.78hi	63.72b	27.19l	21.34c	1.90b	10.36h
	+NPK	0.27a	3.00gh	22.32h	73.31f	3.15h	0.48cd	18.7ef
	+NPK+COMP	0.36a	9.61b	44.35e	70.46g	17.24d	0.00d	20.23de
5% FA	-NF	0.00a	6.00cde	45.41e	76.38e	16.58d	0.09d	20.83de
	+COMP	0.18a	5.45cdef	22.58gh	53.36i	7.46g	0.00d	24.66abc
	+NPK	0.11a	12.45a	54.24c	55.68h	24.78b	1.61bc	26.23a
	+NPK+COMP	0.00a	6.96c	48.43d	72.25fg	16.81d	1.24bcd	24.95ab
10% FA	-NF	0.04a	6.38cd	61.64b	102.85a	11.83ef	3.86a	22.35cd
	+COMP	0.00a	6.86c	63.35b	82.49d	13.38e	3.56a	23.40bc
	+NPK	0.00a	4.37efg	47.66d	50.27j	7.15g	3.43a	14.08g
	+NPK+COMP	0.01a	2.92gh	24.58g	35.52k	7.51g	1.60bc	17.80f
15% FA	-NF	0.00a	3.26gh	22.74gh	33.46k	6.29g	1.05bcd	15.37g
	+COMP	0.00a	12.75a	32.25f	49.47j	10.45f	2.05b	22.42cd
	+NPK	0.00a	4.02fg	5.80i	53.71hi	10.47f	1.29bcd	20.29de
	+NPK+COMP	0.00a	4.71defg	21.54h	91.26b	12.41ef	1.94b	22.42cd
P values								
FA		0.545NS	0.000***	0.000***	0.000***	0.000***	0.000***	0.000***
Fertilizer		0.981NS	0.000***	0.000***	0.000***	0.000***	0.000***	0.000***
FA x Fertilizer		0.467NS	0.000***	0.000***	0.000***	0.000***	0.000***	0.000***
Maximum allowable levels in vegetables (mg kg ⁻¹ , d.w.)		0.30 ²	2.3 ³	40 ³	30-500 ³	5.0 ³	0.30-0.50 ³	60 ³

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. *-significant; ** highly significant; *** very highly significant; NS-non-significant.

²Yanez et al. 2019

³Latif et al. 2018

in Selebi-Phikwe soils except for As. Specifically, the concentration of As was highest in 0% FA+ no fertilizer while all others had lower concentration but statistically similar to the control. However, the addition of 10% FA and 15% FA resulted to concentration of As increased by beyond detection limit. The concentration of Cr was significantly increased due to application of fly ash and fertilizers with highest concentrations was recorded in 15FA+ compost. For treatments with FA, lowest Cr concentration was observed in 10%FA+NPK+Comp. The concentration of Cu was highest in 0FA- NF followed by 0FA+compost while the addition of compost resulted to further

reduction in the concentration of Cu compared to its counterparts in 5% FA. In 10%FA+NPK+Comp and 15%FA+NPK+Comp, a reduction of 3-fold was observed based on the control. The concentration of Mn ranged from 33.46 to 88.37 mg kg⁻¹ and the highest concentration was obtained in 10%FA-NF. The addition of 15FA alone resulted to reduction of 2.64 folds compared to the control. Except for 0%FA+comp, 10%FA+NPK+Comp and 15%FA alone, all other treatments had Mn concentration in shoots above the maximum tolerable levels for human consumption of vegetables. The Ni concentration the shoots of spinach was significantly reduced due to either the application of FA or the fertilizer. However, the recorded concentrations of Ni in shoots are still above the maximum tolerable levels for vegetables. The addition of FA resulted to reduction of Ni up to 6-fold based on the control. The concentration of Pb in shoots of spinach was significantly reduced by 10%FA and to a lesser extent by 15%FA as compared to the control regardless of the fertilizer applied. The Zn concentration was highest in 5%FA+NPK and most of the concentrations are above the max allowable levels for vegetables except for treatments from 0%FA+Comp and 10%FA+Comp.

These results indicate the complexity of multi-metal dynamics in plant-soil continuum. Considering the overall heavy metal accumulation patterns, it appeared that application of 5-10% FA in combination with compost will have the lower amount of metals that will be accumulated in shoots of spinach. This could be attributed to higher yield that may have diluted the concentration of these metals in shoots.

Heavy Metal contents in the roots of spinach

Table 4.16 shows heavy metal concentration in the roots of spinach grown in Selebi-Phikwe agricultural soil as affected by fly ash and nutrient sources. There is a significant

interaction effect for on all heavy metal contents. Specifically, As concentration was highest in 0%FA+NPK amounting to 1.64 mg kg^{-1} while all other treatments have 0.0 to 0.9 mg kg^{-1} values. The Cr concentration ranged from 22.72 to 53.30 mg kg^{-1} and had the highest concentration in 0FA+NPK. The addition of 5% and 10% fly ash resulted significant reduction of Cr in roots of spinach specially at 5%FA rate. Similar to Cr, the concentration Cu in roots was significantly reduced by FA application. The concentration of Mn was significantly high in treatments with 0FA and such concentration was significantly reduced by the application of 5 to 15% FA. Lowest Mn reduction in roots was observed in treatments with 15%FA. The Ni and Pb concentrations in roots were also reduced significantly by FA application especially at 10 to 15% FA. The Zn concentration in roots ranged from 31.88 to 92.70 mg kg^{-1} . Treatments receiving compost have significantly higher Zn content than their counterpart in each FA application rates.

Except for arsenic, the concentration of Cr, Cu, Mn, Ni, Pb, and Zn were higher in roots compared to shoots of spinach indicating low translocation to above ground part especially in no-amended Selebi-Phikwe soil. Fly ash in combination with compost had reduced the concentration in roots and eventually the translocation to shoots.

4.4.2.2. Heavy metal concentration in the tissues for Rape grown in Selebi Phikwe soil

Heavy Metal contents in the shoots of rape

There is a highly significant interaction between FA and fertilizer in the heavy metal contents of shoots of rape except for (see Table 4.17). The concentration of As observed a statistically similar concentration to the control with values ranging from 0.01 to 0.35 mg kg^{-1} . The Cr, Cu, Mn, Ni, and Pb concentration in shoots of rape was significantly reduced by the application of 5 to 15% FA with slight variability due to the type of fertilizer applied. The concentration of Zn

Table 4.16. Heavy metal concentration in the roots of Spinach grown in soils from Selebi-Phikwe as influenced by fly ash amendments and different source of fertilizer.¹

Treatment Combination		Heavy Metal Concentration in Roots (mg kg ⁻¹)						
FA Levels	Fertilizer	As	Cr	Cu	Mn	Ni	Pb	Zn
0% FA	-NF	0.00b	47.00a	156.84a	107.34b	22.38b	12.18a	33.64d
	+COMP	0.00b	42.28a	133.62a	88.62c	23.70b	11.20a	63.87b
	+NPK	1.64a	53.30a	164.22a	132.60a	21.32b	12.62a	31.88d
	+NPK+COMP	0.00b	49.31a	142.15a	124.20a	29.30a	10.12a	48.30c
5% FA	-NF	0.03b	22.72c	98.31b	110.30b	18.15c	8.69b	32.46d
	+COMP	0.04b	28.77c	74.60c	97.36bc	17.22c	9.77b	74.24ab
	+NPK	0.00b	24.63c	96.34b	82.50c	14.28d	7.96b	38.20d
	+NPK+COMP	0.09b	26.14c	102.30b	118.34b	18.77c	6.95b	64.80b
10% FA	-NF	0.00b	31.12b	76.86c	96.17bc	13.83d	4.12c	48.67c
	+COMP	0.00b	32.56b	89.57c	82.22c	15.32c	4.24c	92.70a
	+NPK	0.06b	28.31c	82.93c	89.17c	15.50c	3.18c	38.49d
	+NPK+COMP	0.00b	29.52b	114.87b	113.60b	17.11c	5.06c	60.62b
15% FA	-NF	0.00b	33.48c	73.87c	64.16d	15.73c	3.35c	38.20d
	+COMP	0.00b	41.68a	82.25c	73.87d	16.85c	2.79c	80.32a
	+NPK	0.00b	34.92b	83.94c	77.92cd	15.40c	4.17c	49.26c
	+NPK+COMP	0.09b	44.11a	99.20b	82.72c	18.31c	4.36c	75.40ab
P values								
FA		0.000** *	0.000***	0.000***	0.000***	0.000***	0.104NS	0.000***
Fertilizer		0.000** *	0.000***	0.000***	0.000***	0.000***	0.011*	0.000***
FA x Fertilizer		0.050*	0.000***	0.000***	0.000***	0.000***	0.000***	0.000***
Maximum allowable levels in vegetables (mg kg ⁻¹ , d.w.)		0.30 ²	2.3 ³	40 ³	30-500 ³	5.0 ³	0.30-0.50 ³	60 ³

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. *-significant; *** very highly significant; NS-non-significant.

²Yanez et al. 2019

³Latif et al. 2018

ranged from 6.47 to 55.39 mg kg⁻¹ and the concentration in treatments receiving compost are significantly higher compared to their counterpart on the same FA rates. Compared to spinach, the concentration of Cr, Cu, Mn, Ni, and Pb were much lower in the shoots of rape. Although the

Table 4.17. Heavy metal concentration in the shoots of rape (2nd crop) grown in soils from Selebi-Phikwe as influenced by fly ash amendments and different source of fertilizer.¹

Treatment Combination		Heavy Metal Concentration in Shoots (mg kg ⁻¹)						
FA Levels	Fertilizer	As	Cr	Cu	Mn	Ni	Pb	Zn
0%FA	-NF	0.26a	28.50a	73.63a	85.34a	17.56a	1.06a	21.59bc
	+COMP	0.13a	23.72b	51.91b	61.04b	16.85a	0.34c	51.73a
	+NPK	0.35a	25.03b	69.76ab	78.97a	17.66a	1.27a	35.46b
	+NPK+COMP	0.15a	23.69b	55.14b	56.54b	16.62a	0.74b	52.79a
5%FA	-NF	0.27a	7.17c	17.27c	32.11c	4.23b	0.74b	17.79c
	+COMP	0.02a	4.42c	12.73c	21.48d	3.58b	0.48c	55.39a
	+NPK	0.10a	4.49c	17.92c	22.16d	4.38b	0.85b	17.95c
	+NPK+COMP	0.32a	3.25d	16.85c	28.26cd	4.36b	0.64bc	52.88a
10%FA	-NF	0.23a	2.96d	14.76cd	31.43c	1.05c	0.30c	8.70d
	+COMP	0.05a	1.69d	17.96c	19.95d	1.63c	0.27c	49.28a
	+NPK	0.07a	2.53d	13.43cd	17.01de	1.61c	0.25c	7.53d
	+NPK+COMP	0.14a	1.17d	10.06d	21.38d	1.55c	0.24c	47.87a
15%FA	-NF	0.23a	1.66d	10.86d	15.51e	1.86c	0.14d	6.47d
	+COMP	0.06a	5.46c	13.09cd	21.95d	1.32c	0.18d	29.10b
	+NPK	0.07a	1.61d	8.79d	19.86d	1.50c	0.15d	8.00d
	+NPK+COMP	0.03a	2.43d	8.88d	27.10cd	1.12c	0.17d	28.36b
P values								
FA		0.477NS	0.008**	0.000***	0.000***	0.000***	0.000***	0.000***
Fertilizer		0.220NS	0.001***	0.000***	0.000***	0.000***	0.000***	0.000***
FA x Fertilizer		0.934NS	0.000***	0.000***	0.000***	0.000***	0.000***	0.000***
Maximum allowable levels in vegetables (mg kg ⁻¹ , d.w.)		0.30 ²	2.3 ³	40 ³	30-500 ³	5.0 ³	0.30- 0.50 ³	60 ³

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. ** highly significant; *** very highly significant; NS-non-significant.

²Yanez et al. 2019

³Latif et al. 2018

concentrations of these metals were above the MAL, there is substantial reduction effected by FA amendments. Such reduction could be attributed to enhance dry matter yield which have diluted the concentration of these metals in plant tissues and the reduction of heavy metal availability in soil due to increase in pH.

HM contents in the roots of rape

There is a highly significant interaction effect of FA and nutrient source in the concentration of heavy metals in roots of rape. This is in exception of the concentration of arsenic (As) which are not significantly affected by both factors (see Table 4.18). The As concentration in roots of rape ranged from 0.00 to 0.13 mg kg⁻¹. The Cr concentration ranged from 27.22 to 63.20 mg kg⁻¹ and had the highest concentration in 0%FA+ compost. The addition of 5 to 15% fly ash resulted significant reduction of Cr in roots of spinach specially at 10FA rate. Similar to Cr, the concentration Cu in roots was significantly reduced by FA application and such reduction was enhanced in treatments with combined NPK and compost application which led to a reduction of 2.12 times less than the control. The concentration of Mn was significantly high in treatments with 0%FA and such concentration was significantly reduced by the application of 5 to 15% FA. Lowest Mn reduction in roots was observed in treatments with 15%FA and those from 10%FA+NPK and 10%FA+NPK+Comp. The Ni and Pb concentrations in roots were also reduced significantly by FA application especially at 10 to 15% FA. The Zn concentration in roots ranged 32.77 to 85.16 mg kg⁻¹. Treatments receiving compost have significantly higher Zn content than their counterpart in each FA application rates.

Similar to spinach, the concentration of Cr, Cu, Mn, Ni, and Pb in the roots of rape was substantially reduced by FA and fertilization. This could be attributed to reduction of the HM availability in soil and subsequent reduced uptake by rape.

Table 4.18. Heavy metal concentration in the roots of rape (2nd crop) grown in soils from Selebi-Phikwe as influenced by fly ash amendments and different source of fertilizer.¹

Treatment Combination		Heavy Metal Concentration in Roots (mg kg ⁻¹)						
FA Levels	Fertilizer	As	Cr	Cu	Mn	Ni	Pb	Zn
0%FA	-NF	0.1333a	62.17a	103.31a	113.22a	26.10a	10.06a	41.22d
	+COMP	0a	63.20a	91.33a	110.72a	26.33a	9.32ab	61.33ab
	+NPK	0.11a	45.83b	89.42a	97.33a	27.31a	11.22a	45.80d
	+NPK+COMP	0.1433a	46.20b	68.48b	103.76a	25.78a	10.33a	72.30b
5%FA	-NF	0a	34.25c	47.32b	73.24b	10.32b	6.78bc	47.22d
	+COMP	0.0733a	32.81c	39.48c	68.36b	9.26b	6.68bc	85.16a
	+NPK	0.0467a	31.33c	43.78b	49.67c	12.30b	7.15b	39.21d
	+NPK+COMP	0a	32.41c	41.83b	58.42b	10.37b	5.92c	72.00b
10%FA	-NF	0.0133a	28.43c	42.87b	70.22b	5.89c	5.84c	38.15d
	+COMP	0a	27.22c	57.33b	54.70b	6.22c	5.83c	63.63c
	+NPK	0a	31.28c	39.44c	47.30c	7.28bc	5.76c	42.88d
	+NPK+COMP	0.0033a	33.54c	48.26b	49.38c	6.30c	6.46bc	68.22b
15%FA	-NF	0a	29.33c	36.27c	39.80c	7.34bc	4.58d	36.50e
	+COMP	0a	31.50c	38.26c	52.70c	6.50c	6.27bc	49.62d
	+NPK	0a	39.28bc	41.68b	49.33c	6.89c	5.80c	32.77e
	+NPK+COMP	0a	30.76c	47.25b	48.20c	8.73b	5.92c	56.12d
P values								
FA		0.545NS	0.000***	0.000***	0.000***	0.000***	0.000***	0.000***
Fertilizer		0.978NS	0.000***	0.000***	0.000***	0.000***	0.000***	0.000***
FA x Fertilizer		0.466NS	0.000***	0.000***	0.000***	0.000***	0.000***	0.000***

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. ** highly significant; *** very highly significant; NS-non-significant.

²Yanez et al. 2019

³Latif et al. 2018

4.4.2.3. Heavy metal concentration in the grain and tissues of corn (*Zea mays*) grown in Selebi Phikwe

HM contents in the kernels of corn

The heavy metal concentrations in the kernels of corn grown in Selebi Phikwe soil were significantly affected by the interaction of fly ash and nutrient sources (see Table 5.9). The As concentration was increased due the application of 15% FA while 10%FA+NPK have As below detection limits. The concentration of Cr ranged from minimum concentration of 0.00 to 38.69 mg

kg⁻¹ and the highest concentration was observed in treatments with 15%FA+ NPK, which is statistically similar to 5%FA+NPK+Comp. The Cu concentration in kernels ranged from 0.00 to 9.41 mg kg⁻¹ with the highest concentration was observed on treatment 15%FA+NPK+Comp. The concentration of Mn significantly varied between treatments and the concentration ranged from 0.00 to 34.04 mg kg⁻¹ and these concentrations are within the acceptable limits for food crops. The concentration of Ni was highest in 5%FA alone which was statistically similar to 15%FA+Comp. treatments with Ni concentration within the acceptable limits include 0%FA with fertilizers, 5%FA and 10%FA with NPK and compost. The Pb concentration ranged from 0.00 to 35.31 mg kg⁻¹ and the highest concentration was observed in treatment 10%FA+NPK. The concentration of Zn was highest in 5% FA+ combination of nutrient sources while all others were statistically similar to each other.

Among the different treatments, 5FA+comp had the lowest heavy metals contents and most of these metals are below the MAL. Other treatments have some other elements that are exceeding the MAL for human consumption. The application of FA at 5% in combination with compost generally decreased the concentration of Cr, Cu, Mn, Ni and Pb.

Heavy metal concentration in the shoots of corn grown in Selebi Phikwe soil

Table 4.20 presents the heavy metal concentration of corn shoots as affected by the interaction of fly ash rates and nutrient sources. Arsenic concentration was significantly increased by application of 15% FA while the other treatments have values statistically similar to the control. The Cr concentration in shoots of corn was reduced by FA and fertilizer application except for treatments 5%FA+NPK+Comp and 10%FA+NPK+Comp. Similarly, the Cu and Ni concentration between different treatments are comparable except for the significantly higher values in

Table 4.19. Heavy metal concentration in the grain of corn (*Zea mays*) grown in Selebi Phikwe soil as affected by fly ash amendment and nutrient sources.¹

Treatments		Heavy metals concentration (mg/kg) for Grain						
FA	Fertilizer	As	Cr	Cu	Mn	Ni	Pb	Zn
0%FA	-NF	0.00c	3.58b	2.50c	2.87d	5.91b	0.00c	1.21c
	+COMP	1.42b	2.09b	4.53b	13.01c	4.75b	0.00c	2.89c
	+NPK	1.36b	7.65b	3.18c	8.443c	4.29c	3.61c	0.00c
	+NPK+COMP	2.89b	12.00b	3.70c	2.29d	1.95c	24.91b	4.15c
5%FA	-NF	3.90ab	16.17b	8.46ab	13.66c	14.53a	0.00c	6.79b
	+COMP	0.64c	1.92b	2.49c	1.63b	1.88c	0.00c	0.00c
	+NPK	1.80b	0.39b	2.54c	7.41c	4.97b	5.40c	0.17c
	+NPK+COMP	0.00c	12.70b	7.71b	17.71b	6.98b	5.38c	9.80a
10%FA	-NF	1.69b	1.78b	1.78ef	22.96b	4.99b	7.14c	3.02c
	+COMP	-	-	-	-	-	-	-
	+NPK	0.00c	0.00b	5.77b	19.09b	6.97b	35.31a	2.80c
	+NPK+COMP	0.80c	2.65b	4.59b	20.68b	2.71c	0.00c	1.38c
15%FA	-NF	5.34a	8.88b	7.95b	8.93c	7.11b	0.00c	4.66c
	+COMP	4.81a	8.53b	6.88b	34.04a	12.40a	0.00c	7.18b
	+NPK	4.40a	38.69a	6.57b	22.92b	6.31b	0.00c	4.27c
	+NPK+COMP	4.94a	0.00b	9.41a	9.96c	3.50c	18.42b	7.18b
P values								
FA		0.038***	0.328NS	0.010***	0.393NS	0.490NS	0.368NS	0.243NS
Fertilizer		0.635NS	0.131NS	0.068NS	0.419NS	0.757NS	0.439NS	0.005***
FA x Fertilizer		0.022*	0.027*	0.011*	0.036*	0.047*	0.027*	0.011*
Maximum allowable levels in vegetables (mg kg ⁻¹ , d.w.)		0.30 ²	2.3 ³	40 ³	30-500 ³	5.0 ³	0.30-0.50 ³	60 ³

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. *-significant; *** very highly significant; NS-non-significant.

-NF = no fertilizer; +COMP=compost; +NPK = with inorganic NPK; +NPK+COMP = combine NPK and compost

²Yanez et al. 2019

³Latif et al. 2018

10%FA+NPK+Comp and 15%FA+NPK+Comp for Cu and in 5%FA+NPK for Ni. The Mn concentration was significantly higher in 5%FA+NPK+Comp and 5%FA alone while other have comparable values with control. Lead concentration was higher in treatments with FA and nutrient

especially in 5%FA alone and 5%FA+Comp. Significantly higher Zn concentration was observed in treatments with compost regardless of the FA rates.

These results would show that corn can accumulate higher amount of As, Cu, and Ni in FA amended soils like this from Selebi-Phikwe as compared to the leafy vegetables spinach and rape but lesser for Cr and Mn. Such differences could be attributed inherent species characteristics. Corn being a monocot tend to accumulate more heavy metals than leafy vegetables (Mirecki et al., 2015).

Heavy metal concentration in the roots of corn grown in Selebi Phikwe soil

Significant interaction effect of FA and fertilizer was observed on the heavy metal concentration in the roots of corn grown in Selebi-Phikwe soils (see Table 4.21). Arsenic concentration was significantly enhanced by FA, but the addition of fertilizers had reduced the magnitude of increase. Highest As concentration was recorded in 15%FA alone while the lowest was in 5%FA+Comp. The Cr concentration in all treatments was almost similar except for a significantly higher values in 15%FA+Comp. The Cu concentration in roots of corn was also increased by FA and fertilizer application especially in 10%FA and 15%FA treatments while the Mn concentration increased by FA application except in treatments 5%FA+NPK, 10%FA+NPK+Comp, and 10%FA+NPK. Nickel concentration was significantly increased in treatments 10%FA+NPK, and 10%FA+Comp as compared to the control while the Zn concentrations was significantly higher in treatments with compost regardless of the FA rates.

These results showed the potential of FA in combination with compost can enhance heavy metal retention in roots of corn and prevent uptake to above ground parts especially into the kernels. However, it should be noted that specific rates and nutrient combination could result in

Table 4.20. Heavy metal concentration in the shoots of corn (*Zea mays*) grown in Selebi Phikwe soil as affected by fly ash amendment and nutrient sources.¹

Treatment combination		Heavy Metal Concentrations of Corn Shoots (mg kg ⁻¹)						
FA	Fertilizer	As	Cr	Cu	Mn	Ni	Pb	Zn
0%FA	-NF	0.79b	17.10b	7.14b	33.78c	6.80b	0.00c	4.24c
	+COMP	0.53b	11.61c	8.25b	27.17c	7.53b	0.00c	10.00ab
	+NPK	0.75b	19.09b	6.12b	28.83c	5.61b	0.00c	8.82c
	+NPK+COMP	0.62b	0.00d	5.54c	0.00d	7.28b	0.65c	13.52a
5%FA	-NF	0.59b	14.90c	7.82b	40.02b	7.36b	2.16a	11.49ab
	+COMP	0.38b	5.68d	5.89b	10.93d	4.69b	2.82a	15.52a
	+NPK	0.76b	5.47d	6.55b	23.44c	10.29a	1.25b	6.82abcd
	+NPK+COMP	0.34b	20.66a	7.49b	50.71a	6.36a	1.75b	11.37ab
10%FA	-NF	0.62b	10.33c	9.88a	16.88c	6.12b	1.42b	5.51c
	+COMP	0.85b	19.36b	7.34b	5.55d	7.29b	0.00c	10.52b
	+NPK	0.60b	10.65c	10.16a	2.62d	7.90b	1.37b	4.86c
	+NPK+COMP	0.09b	22.03a	4.43c	15.23c	5.74b	1.45b	10.40b
15%FA	-NF	2.19a	13.86c	7.10b	14.18c	8.97b	1.07b	14.27a
	+COMP	2.01a	5.68d	8.44b	16.55c	3.34b	1.12b	0.77c
	+NPK	2.41a	0.00d	5.40c	25.21c	6.53b	1.27b	10.42b
	+NPK+COMP	2.57a	11.85c	9.73a	23.22c	8.23b	0.00c	4.42c
Pvalues	FA	0.322NS	0.401NS	0.459NS	0.126NS	0.831NS	0.378NS	0.002***
	Fertilizer	0.608NS	0.786NS	0.951NS	0.617NS	0.691NS	0.517NS	0.845NS
	FAxFertilizer	0.035*	0.044*	0.025*	0.006*	0.042*	0.048*	0.041*
Maximum allowable levels in vegetables (mg kg ⁻¹ , d.w.)		0.30 ²	2.3 ³	40 ³	30-500 ³	5.0 ³	0.30-0.50 ³	60 ³

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. *-significant; *** very highly significant; NS-non-significant.

-NF = no fertilizer; +COMP=compost; +NPK = with inorganic NPK; +NPK+COMP = combine NPK and compost

²Yanez et al. 2019

³Latif et al. 2018

specific accumulation pattern for each metal as a product of the interaction of the spatial and temporal dynamic of metals in rhizosphere-root interphase and the physiological response of plant on this specific environment.

Overall, based on the concentration of heavy metals on edible parts of different species planted sequentially in Selebi-Phikwe soils, treatments from 10%FA+NPK+Comp had the greatest number of metals that are below MAL across different species. Such reduction could be account for enhanced growth in these crops due to the presence of essential nutrients provided by FA and NPK fertilizer as well as the beneficial effect of compost on nutrient availability and on soil biological properties. The enhancement of growth could lead to dilution of metals in the plant tissues and improve the capacity of plants against heavy metal stress. This is evident in the results presented here indicating that the heavy metal concentrations are remarkably lower in plants with high biomass yield.

4.5. Impact of Fly ash Amendments and Nutrient Sources on the Chemical Properties of Soils

4.5.1. pH and Electrical Conductivity of Tswapong Soils

Table 4.22. presents the pH and EC of Tswapong soil collected at different sampling period during the first crop, second crop and third. Only the main effect of FA was observed on the pH of soil during the October 2019 and the May 2020 sampling period. A significant interaction effect of FA and fertilizer was observed on the EC during the October 2019, February 2020, and May 2020 sampling. Regardless of the nutrient sources, the pH of the soil with FA at 5%, 10%, and 15% levels were significantly higher than the control but statistically similar. Soil pH without FA was 7.60 and was increased to 8.00 due to 5% FA, 8.07 for 10% FA, and 8.07 for 15% FA during October 2019.

In February 2020, the pH of the soil without FA slightly increased to 7.97 and FA amendments further increased the pH to 8.33 and 8.43 for the 10FA and 15FA respectively. This

Table 4.21. Heavy metal concentration in the roots of corn (*Zea mays*) grown in Selebi Phikwe soil as affected by fly ash amendment and nutrient sources.¹

Treatment combination		Heavy Metal Concentrations (mg kg ⁻¹)						
FA	Fertilizer	As	Cr	Cu	Mn	Ni	Pb	Zn
0%FA	-NF	3.75c	3.02b	3.77c	2.90c	2.85c	0.00b	0.57c
	+COMP	4.13c	7.37b	4.11c	4.30c	3.91c	4.83b	13.33b
	+NPK	7.46c	7.02b	5.76c	16.35b	6.40c	0.00b	4.25c
	+NPK+COMP	10.79b	0.66b	6.98c	10.18b	8.86c	0.00b	13.68b
5%FA	-NF	8.79b	3.13b	6.49c	20.52b	6.19c	7.64a	6.81c
	+COMP	1.63c	5.19b	1.10c	9.56b	1.14c	0.00b	11.96b
	+NPK	10.05b	1.68b	9.92c	2.60c	3.43c	7.45a	10.29c
	+NPK+COMP	8.84b	0.00b	6.27c	21.43b	9.10c	3.83b	15.28b
10%FA	-NF	10.74b	6.05b	32.38c	59.23a	0.36c	8.15a	6.66c
	+COMP	9.97b	4.11b	67.58a	13.99b	13.04b	2.55b	24.43a
	+NPK	12.76a	5.74b	66.97a	3.63c	18.59a	9.96a	14.29b
	+NPK+COMP	6.11c	1.95b	20.64c	1.20c	0.94c	5.15b	20.00a
15%FA	-NF	14.54a	6.21b	65.72a	14.07b	10.02b	6.37ab	9.34c
	+COMP	14.12a	17.54a	7.03c	11.29b	21.47a	9.27a	14.75b
	+NPK	9.46b	2.23b	28.80c	24.38b	8.67c	7.91a	8.92c
	+NPK+COMP	8.83b	1.61b	50.99b	17.60b	0.00c	8.76a	17.92ab
P-values	FA	0.217NS	0.357NS	0.035*	0.792NS	0.278NS	0.709NS	0.002***
	Fertilizer	0.155NS	0.086NS	0.948NS	0.553NS	0.0189NS	0.921NS	0.124NS
	FAx Fertilizer	0.029*	0.034*	0.050*	0.031*	0.029*	0.034*	0.020*
Maximum allowable levels in vegetables (mg kg ⁻¹ , d.w.)		0.30 ²	2.3 ³	40 ³	30-500 ³	5.0 ³	0.30-0.50 ³	60 ³

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. *-significant; *** very highly significant; NS-non-significant.

-NF = no fertilizer; +COMP=compost; +NPK = with inorganic NPK; +NPK+COMP = combine NPK and compost

²Yanez et al. 2019

³Latif et al. 2018

data showed the ability of FA to increase the pH of the soils like the Tswapong soil, and that this increases beyond 8.0 could lead to nutrient imbalance in soils and result to malnutrition of plants. This data further indicates that lower rates should be added so that soil pH will not increase beyond optimum pH for crops.

Table 4.22. The pH and EC of Tswapong soil collected during the first crop and second crop as influenced by fly ash amendments and different sources of fertilizer¹ (dS m⁻¹).

Treatment Combinations		pH			EC (dS m ⁻¹)		
FA	Fertilizer	October 2019	February 2020	May 2020	October 2019	February 2020	May 2020
0%FA	-NF	7.60b	7.83a	7.97b	0.08e	0.07g	0.10df
	+COMP	7.63b	8.00a	7.73b	0.08e	0.07g	0.07f
	+NPK	7.67b	8.13a	7.57b	0.08e	0.06g	0.06f
	+NPK+COMP	7.17b	7.8a	7.63b	0.07e	0.04g	0.09f
5%FA	-NF	8.00a	8.23a	7.97ab	0.12d	0.07g	0.08f
	+COMP	7.97a	8.3a	7.80ab	0.13d	0.10f	0.13d
	+NPK	8.37a	8.47a	8.47ab	0.24d	0.10f	0.16d
	+NPK+COMP	8.37a	8.53a	8.50ab	0.16d	0.10f	0.15d
10%FA	-NF	8.07a	8.4a	8.33a	1.42b	0.17e	0.29c
	+COMP	8.23a	8.5a	8.50a	0.64c	0.11f	0.16d
	+NPK	7.97a	8.3a	8.30a	1.26b	0.29e	0.31c
	+NPK+COMP	8.03a	8.37a	8.47a	1.01b	0.18e	0.17d
15%FA	-NF	8.07a	8.17a	8.43a	2.06a	1.11a	0.42b
	+COMP	8.37a	8.47a	8.47a	0.71c	0.63c	0.32c
	+NPK	8.03a	8.17a	8.10a	1.91a	0.94b	1.68a
	+NPK+COMP	8.07a	8.40a	8.40a	1.30b	0.42d	0.49b
P values							
FA		0.000***	0.058NS	0.002**	0.000***	0.001**	0.008**
Fertilizer		0.97NS	0.893NS	0.964NS	0.027*	0.017*	0.018*
FA x Fertilizer		0.989NS	1.00NS	0.983NS	0.029*	0.018*	0.039*

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. *-significant; *** very highly significant; NS-non-significant.

-NF = no fertilizer; +COMP=compost; +NPK = with inorganic NPK; +NPK+COMP = combine NPK and compost

The soil EC was significantly increased by FA and fertilizer during the three-sampling period. In October 2019, the EC in treatments with 15%FA and 10%FA was 7.7 to 24.8 times higher than the control while the 5%FA increased more than 1.4 times to 2.8 times than the control. On February 2020, the EC has substantially decreased in all treatments but similar to the 4WAP, the values from treatments with FA and fertilizers are much higher than the control. Treatments in

15%FA have EC within a range of 416.6 to 1106.67 mS cm⁻¹ while those in 10FA had EC ranged from 113.33 to 276.67 mS cm⁻¹. On May 2020, treatments with FA have significantly higher EC than those without FA especially in 15%FA+ inorganic NPK and 10%FA+ inorganic NPK. The EC in 15FA amended treatments ranged from 320 to 1680 mS cm⁻¹ while in 10%FA and 5%FA ranged from 83.33 to 313.33 mS cm⁻¹.

These results indicate how FA could potentially increase the EC due to high amount of readily soluble minerals and elements. Surge in EC could be detrimental to plants but as shown in the data, EC will be stabilized at lower values several weeks after incorporation of amendments. This data will imply that careful consideration should be taken in the timing of FA incorporation into the soil especially in soils like Tswapong. These data will also underscore the benefits that can be derived from compost in regulating the EC and the risk associated with synthetic fertilizer in sudden EC surges.

4.5.2. pH and Electrical Conductivity of Selebi-Phikwe

Table 4.23 presents the pH and EC of Selebi Phikwe soils collected at different sampling period during the first crop, second crop and third crop. Main effect of FA was observed on pH of soil in all sampling period while an interaction effect of FA and nutrient source was observed on the EC of soils at all sampling periods. Specifically, the pH of soil with FA at 5%, 10% and 15% levels were significantly higher than the control but statistically similar to each other. Regardless of the nutrient amendments, the pH increased from 5.03 to 6.93 due to 5%FA, 7.93 for 10%FA and 8.10 in 15%FA during the October 2019 sampling. In February 2020 sampling, slight increase in pH in all treatments were observed including the 0%FA with a pH of 6.37, 7.87 for treatments receiving 5%FA, 8.40 for treatments receiving 10%FA and 15%FA. In May 2020, the pH was

Table 4.23. The pH and EC of Tswapong soil collected during the first crop and second crop as influenced by fly ash amendments and different sources of fertilizer ¹ (dS m⁻¹).

Treatment Combinations		pH			EC (dS m ⁻¹)		
FA	Fertilizer	October 2019	February 2020	May 2020	October 2019	February 2020	May 2020
0%FA	-NF	7.60b	7.83a	7.97b	0.08e	0.07g	0.10df
	+COMP	7.63b	8.00a	7.73b	0.08e	0.07g	0.07f
	+NPK	7.67b	8.13a	7.57b	0.08e	0.06g	0.06f
	+NPK+COMP	7.17b	7.8a	7.63b	0.07e	0.04g	0.09f
5%FA	-NF	8.00a	8.23a	7.97ab	0.12d	0.07g	0.08f
	+COMP	7.97a	8.3a	7.80ab	0.13d	0.10f	0.13d
	+NPK	8.37a	8.47a	8.47ab	0.24d	0.10f	0.16d
	+NPK+COMP	8.37a	8.53a	8.50ab	0.16d	0.10f	0.15d
10%FA	-NF	8.07a	8.4a	8.33a	1.42b	0.17e	0.29c
	+COMP	8.23a	8.5a	8.50a	0.64c	0.11f	0.16d
	+NPK	7.97a	8.3a	8.30a	1.26b	0.29e	0.31c
	+NPK+COMP	8.03a	8.37a	8.47a	1.01b	0.18e	0.17d
15%FA	-NF	8.07a	8.17a	8.43a	2.06a	1.11a	0.42b
	+COMP	8.37a	8.47a	8.47a	0.71c	0.63c	0.32c
	+NPK	8.03a	8.17a	8.10a	1.91a	0.94b	1.68a
	+NPK+COMP	8.07a	8.40a	8.40a	1.30b	0.42d	0.49b
P values							
FA		0.000***	0.058NS	0.002**	0.000***	0.001**	0.008**
Fertilizer		0.97NS	0.893NS	0.964NS	0.027*	0.017*	0.018*
FA x Fertilizer		0.989NS	1.00NS	0.983NS	0.029*	0.018*	0.039*

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. *-significant; *** very highly significant; NS-non-significant.

-NF = no fertilizer; +COMP=compost; +NPK = with inorganic NPK; +NPK+COMP = combine NPK and compost

similar to that of the February 2020 sampling where the treatments receiving FA have almost similar values within the range of 8.27 to 8.50 regardless of the nutrient source.

Application of fly ash at 5% rate effectively increased the pH of Selebi-Phikwe near neutral and above this rate caused to increase in the pH to alkaline condition which may be detrimental to nutrient balance. The data demonstrated that at longer time after incorporation, the pH of the soil further increased indicating the slow but continues reaction of the acid neutralizing capacity of the

fly ash (Harper and Mbakwe, 2020). Based on this observation, a lower rate of FA amendments could be desirable in increasing the pH of Selebi-Phikwe soil.

In October 2019, the EC of the soils significantly increased due to FA amendments and the magnitude of increase is proportional to the rate of FA applied. All treatment combination under the 15%FA has statistically similar values within a range of 1923 to 2223 $\mu\text{S cm}^{-1}$ and are significantly higher compared to other treatments. This is followed by treatments with 10%FA with EC range from 1113.33 to 1843.33 $\mu\text{S cm}^{-1}$ and those from 5%FA with EC range from 1010 to 1603 $\mu\text{S cm}^{-1}$. Application of compost, NPK and combination at 0%FA also increased the EC to 273, 553 and 656 $\mu\text{S cm}^{-1}$, respectively. In February 2020, the EC in all treatments declined substantially within the range of 86.67 to 436.67 $\mu\text{S cm}^{-1}$. Higher values were observed in treatment with 10%FA and 15%FA compared to those with 5%FA and 0%FA. In May 2020, treatments with FA have significantly higher EC than those without FA especially in 15%FA +NPK and 10%FA+compost. The EC in FA amended treatments ranged from 150 to 763.33 $\mu\text{S cm}^{-1}$.

Application of FA increased the EC of Selebi-Phikwe soil which could be attributed to the soluble mineral and elemental contents of FA. Application beyond 5% FA increased the EC of the Selebi-Phikwe soil beyond the acceptable limits of agricultural soils (200 mS cm^{-1}) which could be detrimental to the growth of plants and salinity build up in soil especially in a semi-arid environment. High salinity results to excessive salt stress in plants that reduce dry matter yield (Gupta et al., 2002).

4.5.3. Effect on heavy metal availability on Tswapong Soils

The available As and Zn contents in Tswapong soil were significantly altered due to the interaction of FA x Fertilizer while the main effects of FA significantly affected the available Cr, Cu, Mn, Ni, and Pb (Table 4.24). The total As concentration in soils was significantly higher in treatments with 5%FA, 10%FA, and 15%FA than those treatments with 0%FA. However, in each FA rate, the As concentration was significantly lower when compost or the combination of compost+ NPK was added as a source of nutrients. On the other hand, the Cu concentration was increased by 10%FA and 15%FA regardless of the presence or absence of fertilizer while the addition of 5%FA has total Cu comparable to those in 0%FA. For the total Pb, a significant difference was only observed between treatments containing 0%FA and 15%FA whereby the average values of the treatments under the 15%FA were 31% higher than those in the 0%FA. Regardless of the FA amendments, the total Zn in soil was significantly higher in treatments with compost by 2.8 times and with combined application of NPK+ compost by 1.9 times than the treatments in 0%FA.

Tswapong soil is a neutral soil with moderate heavy metal contents just below the acceptable limits for agricultural production except for Cr. The addition of FA from 5-15% substantially reduce the available fraction of these metals in soils. Several studies have shown the effect of fly ash on heavy metal availability. In soil and these were attributed to the ability of FA increase in pH which have facilitated the formation of additional negative charges in the soil matrix, inducing precipitation of some heavy metal cations especially when pH are above 7.5 and the presence of CO and MgO, and silicate in fly ash that could form insoluble compounds with metals in soils (Ultra, 2020; Manyiwa and Ultra, 2021; Ultra, 2021).

Table 4.24. The extractable heavy metal contents of Tswapong soil amended fly ash and different sources of fertilizer 8 weeks after planting.¹

Treatment		CaCl ₂ Extractable Heavy Metals in Soils at 8WAP (mg/kg)						
FA Levels	Fertilizer	As	Cr	Cu	Mn	Ni	Pb	Zn
0%FA	-NF	0.21e	6.35a	1.10a	4.85a	2.36a	0.24a	0.26d
	+COMP	0.22e	5.98a	1.02a	4.23a	1.99a	0.11a	2.75a
	+NPK	0.32d	6.19a	0.89a	4.85a	2.06a	0.17a	0.33d
	+NPK+COMP	0.19e	6.18a	1.21a	5.13a	2.01a	0.14a	1.51c
5%FA	-NF	0.49c	3.40b	0.80b	3.01b	1.44b	0.13b	0.27d
	+COMP	0.32d	2.76b	0.73b	2.37b	1.22b	0.06b	3.75a
	+NPK	0.32d	3.40b	0.69b	3.01b	1.44b	0.03b	0.25d
	+NPK+COMP	0.24d	3.08b	0.45b	3.19b	1.33b	0.02b	2.51b
10%FA	-NF	0.68b	1.83c	0.10c	1.16c	0.52c	0.03b	0.27d
	+COMP	0.33d	1.68c	0.11c	1.51c	0.29c	0.03b	2.72a
	+NPK	0.43c	1.32c	0.10c	1.16c	0.52c	0.01b	0.27d
	+NPK+COMP	0.27d	1.93c	0.10c	1.34c	0.40c	0.03b	1.51c
15%FA	-NF	0.92a	1.23d	0.12c	1.32c	0.16d	0.01c	0.27d
	+COMP	0.43c	1.16d	0.13c	1.65c	0.14d	0.00c	3.76a
	+NPK	0.63b	1.23d	0.10c	1.32c	0.16d	0.01c	0.24d
	+NPK+COMP	0.45c	0.92d	0.14c	1.48c	0.15d	0.00c	2.51b
P values								
FA		0.023*	0.047*	0.011*	0.018*	0.011*	0.021*	0.562NS
Fertilizer		0.046*	0.639NS	0.374NS	0.339NS	0.332NS	0.459NS	0.018*
FA x Fertilizer		0.048*	0.732NS	0.611NS	0.413NS	0.428NS	0.622NS	0.036*
Critical Limit for soils		20 mg/ kg	150 mg/ kg	100-150 mg/ kg	400 mg/ kg	25-50 mg/ kg	90 mg/ kg	150-500 mg/ kg

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. ** highly significant; *** very highly significant; NS-non-significant.

-NF = no fertilizer; +COMP=compost; +NPK = with inorganic NPK; +NPK+COMP = combine NPK and compost

4.5.4. Effect on heavy metal availability on Selebi-Phikwe soils

Table 4.25 presents the available fraction of heavy metals in Selebi Phikwe soil. Extractable As, Cr, Mn, and Pb were significantly affected by the main effect of FA while an interaction effect of FA and nutrient sources significantly affected the concentrations of extractable Cu and Ni and a main effect due to fertilizer was observed on Zn.

Regardless of the fertilization, the extractable As and Cr were significantly higher in treatments with FA compared to the 0%FA. The extractable As in 10FA and 15%FA was between 0.32 to 0.38 mg kg⁻¹ while in 5%FA, the concentration ranged from 0.23-0.28 mg kg⁻¹. The extractable Cr was highest in 15%FA followed by 10%FA and 5%FA and the lowest was the 0%FA treatments. The extractable Mn and Pb was significantly reduced by FA application and much lower concentrations were observed in 10%FA and 15%FA. The extractable Cu and Ni was significantly reduced by FA especially at 10% and 15% FA rates whereas Zn was higher in treatments with compost regardless of the FA rates.

Similarly, to the effect of FA on heavy metal availability in Tswapong soil, its application in Selebi-Phikwe had also resulted to substantial reduction of available heavy metals in soil despite the appreciable heavy metal contents of FA. FA has been used to stabilized heavy metal mobility in mine-affected soils and mine tailings because of its ability to neutralized acidity (Kumpiene et al., 2007; Tsang et al., 2014). The Cu and Pb availability and mobility in soil was reduced by the addition on coal fly ash and natural organic matter (peat) by 98.2% for Cu and by 99.9% for PB, and the leachability was reduced by two orders of magnitude Based on the untreated soil in the field lysimeters (Kumpiene et al. 2007). Column leaching experiments of Tsang et al. (2014) revealed that coal FA was more efficient than limestone and bentonite amendments for As stabilization even under continuous leaching of acidic solution, which was attributed to high-affinity adsorption, co-precipitation, and pozzolanic reaction of coal fly ash. Whereas the same experiment has shown that carbonaceous materials are needed to stabilize Cu together with co-application of FA. Overall, the use of fly ash in agricultural soils has been shown to be beneficial in improving soil quality and crop yield, however, should be properly evaluated to check for

Table 4.25. The extractable heavy metal contents of Selebi-Phikwe soil amended fly ash and different sources of fertilizer 8 weeks after planting.¹

Treatment		CaCl ₂ Extractable Heavy Metals in Soils at 8WAP (mg/kg)						
FA Levels	Fertilizer	As	Cr	Cu	Mn	Ni	Pb	Zn
0%FA	-NF	0.18c	2.31c	8.09a	4.70a	2.54a	2.16a	2.87a
	+COMP	0.19c	2.17c	7.89a	4.04a	2.39a	2.15a	4.64a
	+NPK	0.14c	2.25c	7.31a	4.08a	1.51b	2.16a	1.88b
	+NPK+COMP	0.16c	2.28c	7.86a	4.24a	2.46a	2.16a	4.2a
5%FA	-NF	0.26b	2.82b	5.95a	2.66b	1.50b	0.28b	0.85c
	+COMP	0.25b	2.72b	5.30a	2.64b	1.35b	0.27b	3.62a
	+NPK	0.23b	2.92b	4.90b	2.67b	1.49b	0.28b	0.87c
	+NPK+COMP	0.28b	2.91b	4.67b	2.65b	1.43b	0.26b	2.26b
10%FA	-NF	0.38a	3.17b	2.63b	1.06c	0.46c	0.16c	0.84c
	+COMP	0.35a	2.96b	1.13c	1.26c	0.32c	0.12c	3.60a
	+NPK	0.38a	3.15b	2.65b	1.05c	0.45c	0.13c	0.84c
	+NPK+COMP	0.33a	3.06b	1.36c	1.03c	0.39c	0.13c	2.22b
15%FA	-NF	0.32a	4.31a	1.43c	0.96c	0.42c	0.10c	0.82c
	+COMP	0.39a	4.19a	1.80c	1.60c	0.28c	0.13c	3.60a
	+NPK	0.35a	3.84a	1.49c	1.59c	0.40c	0.13c	0.80c
	+NPK+COMP	0.38a	3.99a	1.09c	1.62c	0.37c	0.11c	2.20b
P values								
FA		0.046*	0.029*	0.033*	0.027*	0.018*	0.036*	0.587NS
Fertilizer		0.511NS	0.567NS	0.519NS	0.523NS	0.611NS	0.501NS	0.007**
FA x Fertilizer		0.517NS	0.511NS	0.051*	0.524NS	0.045*	0.510NS	5.82NS
Critical Limit for soils		20 mg/ kg	150 mg/ kg	100-150 mg/ kg	400 mg/ kg	25-50 mg/ kg	90 mg/ kg	150-500 mg/ kg

¹Means in a column followed by the same letter (s) are not significantly different from each other based on Tukey's Test at 5% level of significance. ** highly significant; *** very highly significant; NS-non-significant.

-NF = no fertilizer; +COMP=compost; +NPK = with inorganic NPK; +NPK+COMP = combine NPK and compost

possible harmful effects on product quality of high concentration of both essential and non-essential elements (Yunusa et al. 2012; Shaheen et al. 2014).

The results presented in this study show for the first time the potential of Morupule B fly ash from Botswana as an agricultural soil amendment. The results showed that application of fly ash from 5% to 15% by weight would increase the dry matter yield of spinach, rape and corn but the maximum increase was obtained at 10%FA in all the crops. This would indicate that a 10% by

weight is the optimum rate of FA application for both Selebi Phikwe and Tswapong soils. The observed increase in DMY could be attributed to the following: Except for nitrogen, fly ash contains P, K, S, Ca, Fe, Cu, Mn, Ni and Zn that are essential for plant (see Table 4.0). These nutrients can help improve the plant growth and development as shown by several studies on rice (Panda et al. 2019; Yu et al. 2019), pumpkin crop (Ahmad et al., 2021), wheat (Kausar, 2007), chickpea (Khan and Saboor, 2012), and potato (Tomar and Khan, 2015). As in previous studies, the results show an improvement in dry matter yield and growth due to FA amendment and can be attributed to increased concentrations of essential which, at certain levels, are beneficial for the use of certain plant species (see Table 4.0). A previous study showed that Pumpkin grown in fly ash amended soils at 10-30% rate have higher growth and yield parameters, chlorophyll, and biochemical contents as well as the proline content (Ahmad et al., 2021). In previous field research, soil modified with 25% fly ash boosted rice seedling growth by up to 30% by weight basis and pumpkin seedling growth by up to 30% by weight basis, the results indicate that application of fly ash beyond 10% result to detrimental effects on the growth and yield of the successive crops grown in the two agricultural soils: Selebi Phikwe and Tswapong (Tswapong) soils. Second, depending on the properties of soil, a higher application rate of FA could be favorable to certain crops and soil quality. For instance, the results showed that at high FA rates of 15% FA, the EC could temporarily increase above the optimum levels which could result in salt stress on plants (Tables 6.2 and 6.3). In pea plants (*Pisum Sativum* L.), short-term salt tension interrupted the growth of the leaf, the osmotic potential and the stomatic conductance decreased which eventually delayed growth (Hernández and Almansa, 2002). The pumpkin grew in soil with the higher doses, i.e., 40% and 50% of fly ash showed a negative effect and reduced the growth, chlorophyll, carotenoid, biochemical content, proline, and yield (Ahmad et al., 2021). Based on a meta-analysis by Shakeel

et al., (2019), higher FA levels increase the availability of heavy metals, which can cause oxidative stress through the formation of reactive oxygen species (ROS). The ROS could damage the DNA, destroy the membrane functional integrity, and disturbs protein activity. The use of fly ash at high rates could lead to nutritional imbalances that disrupt physiological processes, such as the reduction of photosynthetic pigments due to the low availability of N and P and the high availability of heavy metals (Shakeel et al., 2019); Varshney. 2019).

The application of fly ash amendment at the right amounts can enhance some of the physicochemical and biological properties of soils (Singh et al. 2016). In a sodic soil, application at 20t ha⁻¹ increased the water holding capacity by 13- 15 %, reduced the bulk density by 20-26%, increased the soil organic carbon, nitrogen, microbial biomass, and population of bacteria and earthworms (Singh et al., 2016). However, high dosage amount of fly ash reduces the microbial activity that is responsible for nutrient mineralization such as nitrification and nitrogen mineralization; and extremely high pH in fly ash retard the biological N fixation (Gupta et al., 2012). Although FA could improve the physical properties that would favor root growth and development, a high application rate can impact roots that come directly in contact with heavy metals and other components in FA that may alter water movement and lower the transpiration rate (Rucińska-Sobkowiak, 2016). For neutral Tswapong soils and Selebi-Phikwe soils, the application of 15% FA had increased the EC above the optimum levels especially during the first 4 to 8 weeks after incorporation.

Additional nutrients slightly increased the yield in the control soils (0%FA) and 5% FA but at 10%FA only those with compost give a superior yield among the different combination during the first crop (spinach), second crop (rape) and third crop (corn) on the two agricultural soils while both the inorganic NPK and the combined inorganic NPK and compost have the best

yield. At 0% to 5%, fertilizer application supplied the nutrients needed for plant use while maintaining favorable EC but at 10% FA, the additional inorganic NPK will contribute to existing high EC beyond the optimal EC levels in the soil which range from 110-570 $\mu\text{S}/\text{cm}$, while compost will have an opposite effect (Tables 4.22 and 4.23). In addition, compost application reduced the availability of excessive essential and non-essential elements from FA that may be detrimental to plant growth by providing an additional adsorption matrix in soil (Table 4.24 and 4.25). Furthermore, the compost application reduced the availability of excessive essential and non-essential elements that can be harmful to plant growth by providing an additional adsorption matrix in the soil.

Tswapong (Tswapong) soil has As, Cu, Mn, Ni, Pb, and Zn levels within the critical limits for agricultural soils while Cr is 3-fold above the suggested limit for agricultural soils by the Portuguese and Canadian regulations. Spinach grown on this soil without FA and fertilizers has As, Cu, Mn, Ni, Pb, and Zn levels below the maximum acceptable level (MAL) for vegetables. The succeeding rape crops have As, Cu, Mn, and Zn levels below the MAL while corn kernels (third crop) have As, Cr, Cu, Mn, Ni, Pb and Zn levels below the maximum acceptable level (MAL) for vegetables. Only the concentrations of Cr and Ni have concentrations above the MAL in spinach while the Cr, Ni, and Pb for rape and this could be attributed to the inherently high concentration in soil while the corn shoots have concentrations above the MAL in As, Cr and Pb (Table 4.4). In spinach, only the concentration of Cr is above the MAL for vegetables which could be attributed to high Cr in soils and considered to be mobile in soils and taken up easily by plants. At 10% FA, the treatments 10%FA+NPK and 10%FA+NPK+Compost has all the metal concentrations in spinach below the MAL while in rape, 10%FA with or without the fertilizers have As, Cr, Cu, Mn Ni Pb, and Zn below MAL. At 15%FA, without the fertilizer, the As, Cr, Cu

Mn and Zn in spinach were below the MAL but the Ni and Pb were above the MAL. At 15%FA, without the fertilizer, the As, Cr, Cu Mn and Zn in spinach were below the MAL but the Ni and Pb were above the MAL. Fertilizer application in 15% FA resulted in Cr and Ni concentrations above the MAL for spinach. For rape, all the concentrations of metal under consideration are below the MAL except for the concentration of Ni in 15%FA-NF. In corn grain grown in Tswapong, 0% FA without nutrient sources have resulted to heavy metal concentration below detection limit. At 5% FA, without fertilizer, the As, Cr, Cu, Ni and Pb concentration were above the above the MAL. At 10% FA, without nutrient sources, a concentration above the MAL in As, Ni and Pb but As, Cr, Ni and Pb was above the MAL in 15% FA.

The addition of fly ash to Selebi Phikwe soil increased the pH and EC which enhanced the uptake of essential nutrients in plants (Dahiya and Budania, 2018). Acidic soils are detrimental to plant growth because it causes oxidative stress on the roots and reduce nutrient availability which lead to stunted growth (Dos Reis et al., 2018). Specifically, the spinach at 0% FA -NF, the concentration of As, Cr, Cu, Ni and Pb were above the MAL while the second crop (rape) has concentrations exceeding the MAL in Cr, Cu, Ni, and Pb. This could be attributed to the inherent toxic elements in Selebi Phikwe acidic soils which rise heavy metal above the MAL. The addition of fly ash reduced the concentration of these metals in the shoots of spinach and the presence of fertilizer had either increased or decreased these metals. FA addition at 5% in spinach, Cr, Ni and Pb is above the MAL for vegetables which could be attributed their high concentration in soils. At 10% FA, Cr, Ni and Pb concentration were above the MAL while at 10% FA only the Cr concentration was above the MAL and is a similar instance with 15% FA.

For the second crop (rape), application of fly ash at 0% FA had concentrations above the MAL for vegetables in Cr, Cu, Ni, and Pb while at 5% FA the concentration above the MAL was

with Cr and Pb concentration. Further addition of fly ash at 10% FA, had the concentration above the MAL only in Cr concentration while 15% FA observed the all the concentrations within MAL range. The addition of fly ash at 10% FA and 15% FA reduced concentration below the MAL is attributed to the dilution effect and the species tolerance to metal toxicity.

The third crop, kernels (corn) at 0% FA- NF observed concentrations above the MAL in Cr and Ni while at 5% FA the addition of fly ash had As, Cr and Ni above the MAL for vegetables. The application of fly ash at 5% FA had As and Pb concentration above the MAL for vegetables while at 15% FA As, Cr and Ni were above the MAL for vegetables. The corn kernels grown in Selebi Phikwe had relatively reduced metal concentration which could be attributed to toxicity tolerance by corn plants.

A general decrease of metals uptake was observed in plants that have high biomass yield and such decrease could either be due to the dilution effect brought about by enhancing growth and biomass yield or reduction of availability due to an increase in pH and presence of compost. The addition of compost could enhance the buffering capacity and neutralize the acidity simultaneously supplying essential nutrients to plants (Sharma and Singh, 2019). Due to microbial load in compost, soil microbial count increases which help translocation of nutrients, increase nutrient availability and consequently absorption by plants (Akmal et al., 2019). Based on the availability of heavy metals, the available As was enhanced by FA but reduced by compost and NPK and the magnitude of reduction was much higher by compost. This increase in As availability is caused by improved negative charges due to the FA and the As content of FA (see Tables 4.13 and 4.14). The decrease in heavy metal availability was caused by a rise in soil pH caused by cationic heavy metal precipitation or increased heavy metal adsorption on soil matrix (Lwin et. 2018, Manyiwa and Ultra. 2021).

Chapter 5

Summary, Conclusion and Recommendations

5.1. Summary

The results presented in this study show for the first time the potential of Morupule B fly ash from Botswana as an agricultural soil amendment. The results showed that application of fly ash from 5% to 15% by weight would increase the dry matter yield of spinach, rape and corn but the maximum increase was obtained at 10%FA in all the crops. This would indicate that a 10% by weight is the optimum rate of FA application for both Selebi Phikwe and Tswapong soils.

Chemical characterization of Morupule FA showed to have an alkaline pH of 8.12 to 8.42, an EC of 2300 to 2370 mS/m, very low organic matter contents of 0.012%, and a liming potential equivalent to 98% CaCO₃. It contained high concentrations of essential elements for plants such P (865 mg kg⁻¹), K (1 676 mg kg⁻¹), S (34 472 mg kg⁻¹), Ca (119 230 mg kg⁻¹), Cu (23 mg kg⁻¹), Fe (36 222 mg kg⁻¹), Mn (796 mg kg⁻¹), Ni (66 mg kg⁻¹), Zn (32 mg kg⁻¹). It also contained some non-essential elements for plants such as As (11 mg kg⁻¹), Hg (8.6 mg kg⁻¹), Ba (614 mg kg⁻¹), Cr (159 mg kg⁻¹), Sr (535 mg kg⁻¹), Zr (374 mg kg⁻¹), and Pb (51 mg kg⁻¹).

Fly ash application from 5 to 15% increased the pH and modified the EC of the soil especially in soils from Selebi-Phikwe and to a lesser extent to Tswapong soils. All rates of FA reduced the available heavy metal concentration in both soils especially Cu, Ni, Cr, Zn, and Pb but increased the concentration of arsenic. Furthermore, the compost application reduced the availability of excessive essential and non-essential elements that can be harmful to plant growth by providing an additional adsorption matrix in the soil.

In Selebi Phikwe soil, the yield of spinach, rape, and corn was increased due to the addition of FA at the rate of 5 to 15%. These yields were enhanced by the addition of compost and NPK, or its combination, especially in treatments with 10% FA. For spinach, treatments with 10FA+comp, 10FA+NPK+Compost, and 15FA+compost had heavy metal concentrations below the maximum allowable limit (MAL) for human consumption; while for rape, only the treatment of 10FA+compost had heavy metals concentrations below MAL. While the kernels harvested from 10FA+compost had heavy metal concentrations below the MAL.

In Tswapong soil, the highest dry matter yield of spinach and rape was obtained in 10FA+NPK+compost, and in 5%FA+NPK+compost for corn. Among the different treatments, spinach and rape grown in 10%FA+NPK alone or combination with compost; and corn kernels from treatment with 15%FA + Compost alone or combination with NPK had low heavy metal concentration, which are below the MAL.

5.2. Conclusion

Morupule fly ash has alkaline pH and contained considerable amount of essential nutrients that can be serve as nutrient source for nutrient deficient soils. However, caution should be strictly observed as the FA also contain some non-essential elements that could be detrimental to soil fertility especially when applied at high volume. The alkalinity of FA is equivalent to 98% calcium carbonate thus could be used as a liming material for acidic soils like those from the Selebi-Phikwe.

The application at 5% FA will not give optimum biomass even with the presence of fertilizer and will have a high concentration of Cr in spinach and corn kernels and Ni in rape shoots beyond the MAL. On the other hand, 15% FA will also result to lesser dry matter yield. These

results indicated the suitability of Morupule Fly Ash as soil amendments in Selebi-Phikwe and Tswapong soils at about 10% by weight.

Fly ash application increased the pH, modified the EC and nutrients availability in soil especially when combined with compost. It has reduced the availability of Cu, Mn, Ni, and Pb but slightly increased the extractable As and Cr in Selebi-Phikwe and Tswapong soils.

Overall, the application rate of 10% FA combined with compost and inorganic NPK in Tswapong and Selebi-Phikwe soils will result to optimum growth of spinach, rape, and corn and the heavy metals contents in the harvested crops were mostly below the MAL and can be safe for human consumption.

5.3. Recommendations

The screen house experiment showed that fly ash can be used as a safe and suitable soil amendment for agricultural and heavy metal contaminated soils. The application rate at 10% FA is recommended to give the best dry matter yield and products that could be safe heavy metal concentration safe for human consumption. However, field verification trials and long-term monitoring experiments on the effect of FA application should be conducted before the adoption of Morupule FA as soil amendments in Tswapong and Selebi-Phikwe soils. Moreover, combined application of nutrient sources with fly ash is recommended to give the optimum yield in crops.

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