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Effects of Different Soil Amendments on Soil pH and Heavy Metals Content in Maize (*Zea Mays* [l.])

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Abstract: Manure from livestock is an important source of nutrient for crop production in the small holder sector. It helps farmers reduce inputs of commercial fertiliser, thereby, increasing the profit margin of the farmer. Not much been done to determine the effects of kraal, goat, poultry and lime on soil pH in Swaziland and nothing has been done to assess if the levels of heavy metals each of these manure contributes to the soil in maize production are within the WHO's safe standards for human consumption. The objectives of the study were to find out the effects of organic and inorganic soil amendments on soil pH and to find the content of heavy metals in maize tissues and grain on maize grown in soil amended with organic and inorganic soil ameliorants. A field experiment, in a randomised complete block design was conducted at Nhlangano Research Station in the 2014/2015 cropping season. Treatments were effective in increasing the soil pH. Goat manure treatment improved soil pH from 4.77 to pH 5.14 whilst the lime treatment improved the soil pH to pH 5.13 at full rate. Chicken manure treatment raised the pH to 4.86 at half rate whilst the goat manure treatment raised soil pH to 4.86 at half rate. The content of Zn was highest in the grain with the goat manure treatment at full rate (0.128 g/kg) and lowest in the chicken manure and lime treatments at half rate (0.025 and 0.021 g/kg). This was due to the high Zn content in the manure. The control treatment had 0.117 g/kg Fe in the grain while the cattle manure treatment at half rate had 0.101 g/kg Fe in the grain. Cadmium was highest in the lime treatment at full rate, goat manure at full rate and both chicken manure treatments (0.022 g/kg Cd). Copper was highest in the control treatment (0.009 g/kg) and lowest in the chicken manure treatment at half rate, goat and lime at full rate (0.003 g/kg). Goat and cattle manure was recommended for amelioration of acid soils.

Keywords: Soil Amendment, Soil pH, Heavy Metals

1. Introduction

Manure from livestock is an important source of nutrient for crop production in the small holder sector. It helps farmers reduce inputs of commercial fertiliser, thereby, increasing the profit margin of the farmer. Nutrients contained in organic manures are released more slowly and are stored for a longer time in the soil, thereby ensuring a long residual effect thus supporting better root development, leading to higher crop yields. Improvements of environmental conditions as well as public health are also important reasons for advocating increased use of organic materials. Maintenance of soil fertility is essential for optimum and sustained production. Inorganic fertilisers can be used to replenish soil nutrients and increase crop yields, but are too costly for the peasant farmers (Ayoola & Makinde, 2008).

The use of mineral fertilisers has been associated with increased soil acidity, nutrient imbalance and soil degradation. This has necessitated research on use of organic manures. The use of organic manure alone, to sustain cropping has been reported to be inadequate due to unavailability in the required quantities and their relatively low nutrient contents. Integrated nutrient management approaches, in which both organic manure and inorganic fertilisers are used, have been suggested. Supply of nutrients from the organic manures can be complemented by enriching them with inorganic nutrients that will be released fast and utilized by crops to compensate for their late start in nutrient release (Ayoola & Makinde, 2008).

Factors contributing to reduced maize production and low yields in Swaziland were listed in a meeting held on the 24th May 2013 by the Crop Promotion Unit as follows: low soil pH, inadequate rainfall that is poorly distributed, poor choice of variety and quality of seeds, low plant population/ha, poor maize storage conditions leading to heavy post harvest losses, marketing of maize, data capture; land area under maize production and yield per unit area (B. Sukati personal communication January, 28, 2014)

Soil pH is a measure of the acidity or basicity of a soil. Soil pH is defined as the negative logarithm (base 10) of the activity of hydrogen ions (H^+ or, more precisely, H_3O + aq) in a solution. In water, it normally ranges from 1 to 14, with 7 being neutral. A pH below 7 is acidic and above 7 is basic. Soil pH is considered a master variable in soils as it controls many chemical processes that take place. It specifically affects plant nutrient availability by controlling the chemical forms of the nutrients. The optimum pH range for most plants is between 5.5 and 7.0, however, many plants have adapted to thrive at pH values outside this range (Leonard, 2012).

The pH of the soil solution is also very important because the soil solution plays a key role in carrying nutrients such as nitrogen (N), phosphorus (P), and potassium (K) to support plant growth. Acid soils are common in the tropics. When the pH is below 4 to 5, growth of crops such as maize is reduced. Desirable pH values for optimum growth of maize are within the range of 6.5 to 7.0 (Nielsen, 2005).

Classification scheme of soils from the Middleveld and Highveld of this country are dominated by acid soils. Plant growth in these ecological zones may be adversely affected by acid infertility factors which includes Al^{3+} phytotoxity (Jones, 1977; Shongwe, 1994; Jones & Murdoch, 1995). Research work done by Dlamini (2000), Bulunga (2006), also indicated that soils from the Middleveld and Highveld of this country are acid in reaction and, therefore, require lime.

Heavy metals" is an inexact term used to describe more than a dozen elements that are metals or metalloids (elements that have both metal and non-metal characteristics). Examples of heavy metals important in agriculture include zinc, copper, iron, chromium, arsenic, cadmium, lead, mercury, and manganese. Generally, heavy metals have densities above 5 g/cm^3. Because they cannot be degraded or destroyed, heavy metals are persistent in all parts of the environment. Human activity affects the natural geological and biological redistribution of heavy metals through pollution of the air, water, and soil. The primary anthropogenic sources of heavy metals are point sources such as mines, foundries, smelters, and coal-burning power plants, as well as diffuse sources such as combustion by-products and vehicle emissions. Humans also affect the natural geological and biological redistribution of heavy metals by altering the chemical form of heavy metals released to the environment. Such alterations often affect a heavy metal's toxicity by allowing it to bio-accumulate in plants and animals, bio-concentration or attack specific organs in the body (Goyer, 1996).

Heavy metals are associated with myriad adverse health effects, including allergic reactions (e.g. beryllium, chromium), neurotoxicity (e.g. lead), nephrotoxicity (e.g. mercuric chloride, cadmium chloride), and cancer (e.g. arsenic, hexavalent chromium). Living organisms require varying amount of heavy metals. Iron, cobalt, manganese, molybdenum and zinc are some of the heavy metals required by humans. Excessive levels can be damaging to the organism. Humans are often exposed to heavy metals in various ways-mainly through the inhalation of metals in the workplace or polluted neighbourhoods, or through the ingestion of food (particularly seafood) that contains high levels of heavy metals or paint chips that contain lead.

The three heavy metals commonly cited as being of the greatest public health concern are cadmium, lead, and mercury. There is no biological need for any of these three heavy metals. Cadmium has many commercial applications, including electroplating and the manufacture of batteries. Exposure to cadmium can occur in the workplace or from contaminated foodstuffs and can result in emphysema, renal failure, cardiovascular disease, and perhaps cancer (Hawkes, 1997).

Animal manures, particularly poultry manure from poultry operations and pig manure contain relatively high concentrations of heavy metals, such as arsenic, copper and zinc. These metals are normally high in manure because concentrations in the diets are high. High concentrations of heavy metals have been documented in runoff water from soils fertilized with animal manure (Goyer, 1996). Heavy metals make a significant contribution to the environment as a result of human activities such as mining, smelting, electroplating, energy and fuel production, power transmission, intensive agriculture, sludge dumping, and melting operations (Hawkes, 1997).

All heavy metals even at low concentration have strong toxic effects and are regarded as environmental pollutants. There is evidence that plants can accumulate heavy metals in their tissues. Metal accumulation by plants is affected by many factors. In general, variations in plant species, the growth stage of the plants and element characteristics control absorption, accumulation and translocation of metals. Furthermore, physiological adaptations also control toxic metal accumulations by sequestering metals in the roots (Moncrif et al., 1999).

2. Materials and Methods

2.1. Experimental Site

The study was conducted on-station. A field experiment was conducted at the Agricultural Research Station of Swaziland, a wing of the Ministry of Agriculture (Nhlangano) during the 2014/2015 growing season to determine the effect of cattle manure, goat manure poultry manure and lime effect on soil pH and heavy metal content in maize. The Nhlangano Research Station is situated in the Highveld agro-ecological zone of Swaziland at 27.07°S, 31.11°E, with an altitude of 1050 meters above sea level. The mean annul temperature for the location is 18°C (Edje & Ossom, 2009). This zone receives an annual rainfall of 955 mm which is well distributed from October to February. The soil of the experimental site is an Oxisol (M-set) of the Malkerns series (Murdoch, 1968), with a pH of 4.75, available phosphorus 22.4 cmol/kg and aluminium 1.07 cmol/kg.

2.2. Plot Layout and Planting

The experiment consisted of nine treatments coded as follows; 1. control, 2. lime at 1.5 t/ha, 3. lime at 3 t/ha, 4. chicken manure at 15 t/ha, 5. chicken manure 30 t/ha, 6. goat manure at 25 t/ha, 7. goat manure 50 t/ha, 8. cattle manure at 25 t/ha 9. cattle manure at 50 t/ha. Hybrid seeds of SC 401, which is an early maturing variety was used in the study. The experiment was laid out in a randomised complete block design with three replicates in a factorial arrangement. Each plot measured 6m x 9m. The inter-row and intra row spacing was 90cm and 30cm. Poultry, goat and cattle manures were collected on the 25th September 2014. Poultry manure was collected from Eagles Nest poultry farm at Malkerns. Eagles nest poultry farm is the largest egg producing company in the country which uses artificially produced feed for egg production. Goat and cattle manures were collected from Dynamic farm in Malkerns. The manures were collected in hessian bags and transported to Nhlangano research station where it was stored under a shed. Land preparation was done on the 5th October 2014. Plot lay out was done on the 6th October 2014. Manures were applied 4 weeks before sowing (14th October 2014) and were incorporated into the soil with the use of hoes and garden forks. The 2:3:2 (22) + Zn fertiliser was applied at 275 Kg/ha (5.5 bags/ha) at sowing. For topdressing L.A.N (28%) was applied at a rate of 125kg/ha (2.5 Bags/ha). Rows were opened using hand hoes with the help of markers to obtain the required spacing for sowing maize. Sowing was done on 24th October 2014. The crop did not emerge well due to prolonged periods of drought in the region. Second sowing was then done on the 25th November 2014. Gap filling operations were done twelve days after planting. The gabs were filled by drilling a hole and then inserting a seed into the hole and the hole was then covered with soil. To keep the crops free from weeds, two hand weeding were carried out during the growing season at 30 and 60 days after sowing. Protective spraying was done to protect the crop from pest and diseases.

2.3. Data Collected and Sample Preparation Procedure

2.3.1. Sample Preparation Procedure

The maize was harvested as green maize on the 28th February 2015 for analysis of the heavy metals content in the grain, leaves and stems. For green maize the crop was harvested at the dough stage. The bottom 10-15 cm part of the stem and matured top leaf were used for analysis of heavy metals in the stems and leaves. Standard sampling procedures were used to determine the soil chemical properties, manure chemical properties and heavy metals content in the grain, leaves and stem. Wet digestion procedure was then used to prepare samples for analysis of heavy metals.

2.3.2. Determination of Soil pH

Before determination of the soil pH, the pH meter was standardized, by first taking the temperature of the solution and set the temperature compensation dial at the experimental temperature. The electrodes were washed with distilled water, wipe of the water with filter paper and introduced to a pH 7.00 buffer solution and then washed again with a pH 4.00 buffer solution for standardisation. This was repeated until constant readings at pH 4.00 and pH 7.00 were recorded. Samples were oven dried at 75°C for 48 hours and were sieved in a 2mm sieve. Duplicate 10g soil samples were then weighed into 50 ml into a beaker and 20ml of 0.01M $CaCl_2$ and the mixture was swirled for 5 minutes using a starring rod, and was allowed to settle. The pH was then taken from the supernatant solution of the mixture.

2.3.3. Determination of Exchangeable Ca, Mg and K

The content of Ca, Mg and K was determined using the method proposed by Lanyon & Heald (1982). Duplicate 10g soil samples were weighed into 250 ml Erlenmeyer flasks and 90 ml of 1N ammonium acetate solution was added. The flasks were placed in an oscillating shaker and shaken for 10 minutes. The content of the flasks was allowed to settle and then filtered through a Whatman No. 42 filter paper into 100 ml volumetric flasks and then were made to volume with the extraction solution. The amount of Mg and Ca was measured by an Atomic Absorption Spectrophotometry (model AA 200) at the appropriate wavelength for each element. Potassium was measured using the Jenway Flame Photometer (model PFP7), the procedure outlined by Knudsen *et al.,* (1982). The nutrient content of the elements was expressed in cmolckg^{-1}.

2.3.4. Determination of Exchangeable Aluminium

In the determination of exchangeable Al, the method outlined by Barnhisel & Berstch (1982) was followed. Duplicate 5g samples were weighed into 250 ml Erlenmeyer flasks and 50 ml of 1N KCl solution was added. The contents of the flasks were then shaken on a mechanical shaker for 30 minutes. After shaking the solution, was allowed to settle and then filtered through Whatman No. 42 filter paper into 50 ml volumetric flasks. The content of Al in the extracts was measured by titration against a 0.01 M NaOH solution. The content of Al in the extracts was then expressed in cmol/kg.

2.3.5. Determination of Phosphorus in the Soil

The ammonium molybdate blue method as outlined by Olsens & Sommers (1982) was followed in the determination of phosphorus in the soil samples from the experimental site. Duplicate 2g dry soil samples were weighed into 50 ml centrifuge tubes and 20 ml of Bray-1 solution were added. The tubes were then mounted on a mechanical shaker and shaken for 5 minutes. The contents of the tubes were centrifuged for 10 minutes on a Kubota centrifuge (model 2010). The supernatant solutions were then filtered through No. 42 Whatman filter paper into 50 ml volumetric flasks. Phosphorus in the extracts was measured using a Biochrom Spectrophotometer (model Libra S12) at a wavelength of 730 nm. The amount of phosphorus in the extracts was expressed in mg/kg soil.

2.3.6. Chemical Analysis of Manures

In the analysis of manure samples, the following elements were determined; Ca, P, K, Mg, Zn, Mn, Cd, Fe, Cu and pH.

2.3.7. Determination of pH of Manure

The method described above was used in the determination of pH of the manures. Duplicate 5g samples of oven dried manure were weighed into 100ml beakers and 20ml of 0.01 M $CaCl_2$ solution was added. The mixtures were swirled for 5 minutes with a glass rod and allowed to equilibrate for 30 minutes. The pH was measured with a Hanna pH meter and expressed as pH $CaCl_2$.

2.3.8. Determination of Ca, P, K, Mg, Zn, Mn, Cd, Pb, Cu, Fe in Manures

The wet digestion procedure was used in the determination of these elements in manures. Duplicate 2.5g manure samples were weighed into 250-ml Erlenmeyer flasks. Ten ml of concentrated sulphuric acid were added into the Erlenmeyer flask and placed on a hot plate. The manures were then digested for 1 hour. The mixture was then allowed to cool and then six drops of hydrogen peroxide were added and the flasks were placed on the hot plate for further digestion. The addition of hydrogen peroxide and heating intervals were done till mixtures cleared up. After that a final addition of hydrogen peroxide was done and the flask was allowed to cool and made up to 50-ml with distilled water.

The content of Ca, Mg, Zn, Fe, Cu, Pd, Cd were determined by Atomic Absorption Spectrophotometry using a Varian Techtron Atomic Absorption Spectrophotometer (model AA200) as proposed by Lanyon & Heald (1982). The appropriate wavelengths for each element were used in measuring the content of each element, which were then expressed as a percentage.

2.3.9. Determination of Ca, P, K, Mg, Zn, Mn, Cd, Cu, Fe in Plant Tissues (Leaves, Stem and Kernels)

A modification of the method outlined by Thomas *et al.,* (1967) was used for the digestion of plant tissues as green maize and dry maize. For the leaves the upper matured leaf was selected for analysis while for the stem, samples were taken from the lower 10 – 15cm from the ground level. Duplicate 0.25g samples for each tissue type were weighed into digesting tubes. Five ml of concentrated H_2SO_4 were added into the digestion tubes and which were placed onto a hot plate for an hour to digest. After that the content in the tubes were slightly cooled and five to six drops of hydrogen peroxide were (reagent grade) added. The tubes were then heated on the hotplate for five minutes. The hydrogen peroxide was added at intervals of five minutes and continuously heated till the contents were clear. Upon clearing, a final hydrogen peroxide addition was made again and the contents heated up a further 30 minutes. The tubes were then allowed to cool and the solutions were transferred into 100 ml volumetric flasks and topped up to volume with distilled water. The samples were then taken for analysis by Atomic Absorption Spectrophotometry using a Varian Techtron Atomic Absorption Spectrophotometer (Model AA 200) as proposed by Lanyon & Healed (1982). Potassium in the extract was determined using a Jenway Flame Photometer (Model PFP7) following the method proposed by Knudsen *et al.,* (1982). Phosphorus was determined calometrically using the ammonium molybdate blue method proposed by Olsens & Sommers (1982). A Biochrom Spectrophotometer (model Libra S12) was used to measure the content of P in the manure extracts. The content of the elements was then expressed as a percentage.

2.4. Statistical Analysis

MSTAT-C computer software package was used for data analysis, calculations of the least significance difference test (LSD) and to separate the significant mean values.

3. Results

3.1. Basic Properties of the Soil and Manures Used in the Study

The textural class of the soil used for the experiment was a loam clay soil. The soil pH results show that the soil used for the trial was very strong acidic. The amount of P in the soil was enough for crop growth since it was above sufficiency levels (20 mg/kg), thus a response to P application is not expected (Table 1). However, this soil has high levels of exchangeable Al and it is very soluble at this pH (4.75), since the pH is below 5.0. The dominant species of Al in the soil solution must have been Al^{3+} at such pH. Potassium in the soil was adequate since the values obtained exceeded the minimum amount suitable for optimum plant growth which is 0.3 m.e/100g. Exchangeable Ca was rather low and Mg adequate.

Table 1. *Some chemical properties of the soil studied.*

pH $CaCl_2$	Exchangeable cations				Available P mg/kg
	Ca cmolc kg^{-1}	Mg cmolc kg^{-1}	K cmolc kg^{-1}	Al cmolc kg^{-1}	
4.75	1.93	4.24	0.44	1.07	22.4

Cattle manure contained high percentage of Mg and K while the percentage of P is the lowest. Among the micronutrients, Fe content is high followed by Cu and Cd was the least in cattle manure (Table 2). The percentage of K and Mg were higher than the other elements in cattle and goat manures with K being the highest. The percentage of P in goat manure was also low and the percentage of Fe was the highest among the micro nutrients in the goat manure (Table 2). Poultry manure contains more Fe and Zn, followed by Cu and Cd was the lowest. Among the macro nutrients Ca was the highest (Table 2).

Table 2. *Chemical properties of manures used in this study.*

Manure type	pH $CaCl_2$	Ca%	Mg%	K%	Mn%	Cd%	Cu%	Zn%	Fe%	Content of P%
Cattle Manure	8.04	0.08	5.80	7.85	0.041	0.003	0.042	0.019	1.57	0.008
Goat Manure	8.65	0.34	2.67	8.58	0.054	0.002	0.046	0.114	1.98	0.008
Chicken Manure	7.64	0.162	0.003	5.33	0.129	0.003	0.009	0.265	0.274	1.66

3.2. Soil pH ($CaCl_2$)

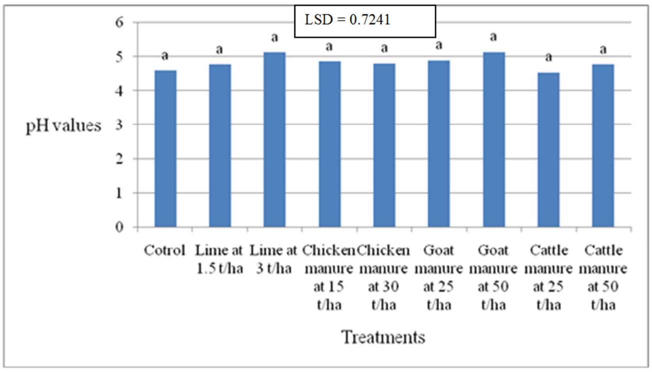

Figure 1. *Post harvest soil pH results for the different treatments.*

Post harvest soil pH results at green maize stage are presented in Figure 1. The results indicate that there was no significant ($P < 0.050$) difference in soil pH among the different treatments. The treatments were statistically similar, however, the greatest positive pH changes from the initial pH of 4.75 were recorded with the goat manure treatment at 50 t/ha and lime treatment at 3 t/ha (5.14 and 5.13). The lowest negative pH changes from the initial soil pH were recorded with the cattle manure treatment at 25 t/ha and the control treatment which gave pH values of 4.54 and 4.60, which was an indication of a slight decrease from the initial pH results of the soil. At half rate (25 t/ha), the lime, chicken and goat manure raised the soil pH from 4.75 to 4.77, 4.86, and 4.9 respectively. At full rates (50 t/ha), the chicken and cattle manure treatment raised the soil pH 4.81 and 4.77 respectively.

3.3. Effect of Ameliorants on the Content of Heavy Metals in the Grain

There were no significant differences ($P < 0.05$) in the content of heavy metals in the grain. The content of Zn was highest in the grain with the goat manure treatment at 50 t/ha (0.128 g/kg) and lowest in the chicken manure and lime treatments at half rate, 1.5 t/kg and 30 t/ha (0.025 and 0.021 g/kg).

Manganese was higher in the chicken manure treatments. At half rate the chicken manure treatment yielded 0.148 g Mn/kg, whilst at full rate the chicken manure treatment resulted in 0.139 g Mn/kg. The control treatment and the goat manure treatment at full rate gave the least content of Mn in the grain. The control had 0.177 g Mn/kg while the goat manure treatment had 0.118 g Mn/kg. From all the treatments, the Mn content was above the recommended daily intake in all foods (0.005 g Mn/kg).

Table 3. *Content of heavy metals in the grain (g/kg).*

Treatment	Zn	Mn	Fe	Cd	Cu
Control	0.031	0.117	0.108	0.017	0.009
Lime at 1.5 t/ha	0.025	0.133	0.045	0.015	0.004
Lime at 3 t/ha	0.035	0.125	0.085	0.020	0.003
Chicken manure at 15 t/ha	0.021	0.148	0.097	0.020	0.003
Chicken manure at 30 t/ha	0.035	0.139	0.057	0.02	0.005
Goat manure at 25 t/ha	0.035	0.130	0.046	0.017	0.005
Goat manure at 50 t/ha	0.128	0.118	0.038	0.020	0.003
Cattle manure at 25 t/ha	0.032	0.139	0.101	0.017	0.004
Cattle manure at 50 t/ha	0.025	0.129	0.063	0.021	0.005
Recommended daily intake	0.004 – 0.181	0.005	0.004 – 0.212	0.0001	0.003 – 0.108
LSD (at alpha 0.05)	0.110	0.055	0.055	0.131	0.145

Iron content was high in the control treatment and cattle manure treatment at half rate. The control had 0.108 g Fe/kg in the grain while the cattle manure treatment at half rate had 0.101 g/kg Fe in the grain. The cattle manure used in the trial had high iron content. Cadmium was highest in the lime treatment at full rate, goat and cattle manure at full rate and both chicken manure treatments. These treatments tallied in cadmium content and they all yielded 0.020 g Cd/kg in the grain.

Copper was highest in the control treatment (0.009 g Cu/kg) and lowest in the chicken manure treatment at half rate, goat manure treatment at full rate and lime treatment at full rate. These treatments produced 0.003 g Cu/kg in the grain. The lime treatment (1.5 t/ha), chicken and goat manure treatments at half rate (15 and 25 t/ha) produced 0.004 and 0.005 g Cu/kg in the grain. The cattle manure treatments (25 and 50 t/ha) produced 0.004 and 0.005 g Cu/kg in the grain respectively.

3.4. Content of Heavy Metals in Leaves

The results indicated that there were no significant (P < 0.05) differences in the content of Fe, Cu, Cd, Zn and Mn in the leaves. Zinc was high in the leaves in plants grown on goat manure at full rate (50 t/ha) (0.128 g/kg). Cattle and goat manure (25 t/ha) treatments produced 0.032 and 0.035 g Zn/kg in the leaves, whilst the lime (3 t/ha) and control treatments produced 0.035 and 0.031 g Zn/kg in the leaves. Lowest contents of Zn were recorded from the lime and cattle manure treatments (1.5 and 50 t/ha). These treatments produced 0.025 and 0.025 g Zn/kg respectively.

Iron was high in all the treatments. The control treatment pooled in Fe content in the leaves (0.305 g Fe/kg). The lime treatment at half rate (1.5 t/ha) and cattle manure treatment at full rate produced (50 t/ha) resulted in 0.214 and 0.202 g Fe/kg in the leaves. The goat manure treatments (25 and 30 t/ha) yielded 0.112 and 0.136 g Fe/kg in the leaves, while the chicken manure treatments (15 and 30 t/ha) produced 0.154 and 0.116 g Fe/kg in the leaves. The lowest amount (0.103 g Fe/kg) was recorded from the cattle manure treatment (25 t/ha).

Table 4. *Content of heavy metals in the leaves (g/kg).*

Treatment	Zn	Mn	Fe	Cd	Cu
Control	0.031	0.114	0.305	0.011	0.007
Lime at 1.5 t/ha	0.025	0.139	0.214	0.009	0.007
Lime at 3 t/ha	0.035	0.117	0.124	0.006	0.013
Chicken manure at 15 t/ha	0.021	0.154	0.096	0.019	0.010
Chicken manure at 30 t/ha	0.035	0.116	0.078	0.014	0.006
Goat manure at 25 t/ha	0.035	0.112	0.141	0.010	0.004
Goat manure at 50 t/ha	0.128	0.136	0.135	0.0115	0.013
Cattle manure at 25 t/ha	0.032	0.103	0.097	0.010	0.010
Cattle manure at 50 t/ha	0.025	0.141	0.202	0.015	0.012
LSD (at alpha 0.05)	0.310	0.055	0.256	0.173	0.154

Manganese was highest in the leaves from the chicken manure treatment at half rate (15 t/ha) (0.154 g/kg Mn). The lime treatments (1.5 and 3 t/ha) produced 0.139 and 0.117 g Mn/kg in the leaves. The goat manure treatments (25 t/ha and 50 t/ha) resulted in 0.112 and 0.136 g Mn/kg in leaves. The cattle manure treatment (25 t/ha) produced 0.130 g Mn/kg, which was the lowest.

Cadmium was higher in both chicken manure treatments and lowest in the lime treatment at 3 t/ha. The chicken manure treatment at half rate yielded 0.002 g Cd/kg in the leaves, while the full rate treatment yielded 0.014 g Cd/kg in the leaves. Cattle and goat manure treatments (25 t/ha) produced 0.010g Cd/kg in the leaves while at full rate (50 t/ha) produced 0.012 g Cd/kg. The lowest amount of Cd was recorded from lime treatments (1.5 and 3 t/ha) (0.009 and 0.006 g Cd/kg) respectively.

The lime treatment, goat and cattle manure treatments at full rate yielded higher quantities of Cu in the leaves. The treatments yielded 0.013, 0.013 and 0.012 g Cu/kg in the leaves. The lime treatment at half rate (1 500 kg/ha) and the control treatment both produced 0.007 g Cu/kg in the leaves. The cattle manure treatments (25 and 50 t/ha) produced 0.010 and 0.012 g Cu/kg in the leaves. The chicken manure treatments (15 and 30 t/ha) yielded 0.01 and 0.006 g Cu/kg in the leaves. The lowest amount of Cu in leaves (0.004g Cu/kg) was recorded with the goat manure treatment (25 t/ha).

3.5. Content of Heavy Metals in Stem

There were no significant (P < 0.05) differences among the treatments in heavy metals content in the stem. However, the LSD results showed that control treatment was significantly similar to the lime treatment (1.5 t/ha) and produced 0.031 g Zn/kg and 0.025 g Zn/kg in the stem. The lime treatment (3 t/ha), chicken manure treatments (15 and 30 t/ha), goat and cattle manure treatments (25 t/ha) and goat and cattle manure treatments (50 t/ha) were significantly similar and produced 0.035, 0.021, 0.035, 0.035, 0.128, 0.032 and 0.025 g Zn/kg in the stem respectively.

Iron content in the stem was highest in the control treatment (0.305 g Fe/kg) in the stem and the treatment significantly similar to the lime treatment (1.5 t/ha), chicken manure treatment (30 t/ha), both goat and cattle manure treatments (25 and 50 t/ha). These treatments produced 0.214, 0.078, 0.141, 0.135, 0.097 and 0.202 g Fe/kg in the stem respectively. The chicken manure treatment (15 t/ha) produced the lowest amount 0.096 g Fe/kg in the stem.

Cadmium was highest in the chicken manure treatment at half rate and the treatment was significantly similar to the chicken manure treatment at full rate. At full rate (30 t/ha) the amount in the stem from chicken manure was 0.014 g Cd/kg and at half rate (15 t/ha) chicken manure produced 0.019 g Cd/kg in the stem. Goat and cattle manure treatments (25 and 50 t/ha) produced 0.010, 0.012, 0.010 and 0.015 g Cd/kg respectively. The control treatment produced 0.011 g Cd/kg whilst the lime treatments (1.5 and 3 t/ha) produced the lowest amounts 0.000 and 0.006 g Cd/kg in the stem respectively.

Copper was highest in the goat manure treatment, lime treatment and cattle manure treatment at full rate. The goat and lime treatment at full rate (50 and 3 t/ha) had 0.013 g Cu/kg in the stem while the cattle manure treatment (50 t/ha) produced 0.012 g Cu/kg in the stem. The lowest quantity of copper was obtained from the goat manure treatment at half rate (0.004 g Cu/kg) in the stem. The chicken manure treatments (15 and 30 t/ha) produced 0.010 and 0.006 g Cu/kg in the stem whilst the control and lime treatment (1.5 and 3 t/ha) produced 0.007, 0.007 and 0.013 g Cu/kg respectively.

Table 5. *Content of heavy metals in stem (g/kg).*

Treatments	Zn	Mn	Fe	Cd	Cu
Control	0.031	0.114	0.305	0.011	0.007
Lime at 1.5 t/ha	0.025	0.139	0.214	0.000	0.007
Lime at 3 t/ha	0.035	0.117	0.124	0.006	0.013
Chicken manure at 15 t/ha	0.021	0.154	0.096	0.019	0.010
Chicken manure at 30 t/ha	0.035	0.116	0.078	0.014	0.006
Goat manure at 25 t/ha	0.035	0.112	0.141	0.010	0.004
Goat manure at 50t/ha	0.128	0.136	0.135	0.012	0.013
Cattle manure at 25 t/ha	0.032	0.103	0.097	0.010	0.010
Cattle manure at 50 t/ha	0.025	0.141	0.202	0.015	0.012
LSD (at alpha 0.05)	0.055	0.197	0.094	0.997	0.145

4. Discussions

4.1. Effect of the Manures on Soil pH

The results showed that there was no significant ($P < 0.05$) difference in soil pH from among the different treatments and all the treatments had a positive effect on soil pH. The treatments were effective in increasing the soil pH. At full rates, the goat manure treatment (at 50 t/ha) and the lime treatment (at 3 t/ha) gave the largest influence on soil pH. The goat manure treatment improved the soil pH from 4.77 to pH 5.14 whilst the lime treatment improved the soil pH to pH 5.13. Manures can increase soil pH through neutralization reaction or through the deprotonation of organic groups (Shongwe, 2013). Manures have high concentrations of OH^- ions as indicated by their high pH. The goat manure used in the study had a pH value 8.65. The high pH in the manure is from the high ammonia content found in the animals' urine. Manures also have a variety of organic groups which are deprotonated and thus have negative charges to adsorb H^+ in the soil solution of acid soils. In addition, during microbial decomposition of incorporated manures, basic cations are released which would raise the initial pH of the soil to a more favourable level for crop production (Pucknee & Summer, 1997). A pH value of 5 or 5.2 is adequate for plant growth in our soils. So this pH values obtained are adequate.

In the lime treatment the high Ca content was probably responsible for the relatively high pH in amended plots. From the liming equation ($CaCO_3 + H_2O \rightarrow Ca^{2+} + HCO_3 + OH^-$), the OH^- reacts with indigenous H^+ or H^+ formed from the hydrolysis of Al^{3+}. Lime addition helps generate OH^- through hydrolysis of the CO_3 component of a liming material. However, liming of acid soils high in exchangeable Al^{3+} might not be a solution since these results in a decrease in the availability of phosphorus (Knudsen et al., 1982). These suggest the use of other materials like the organic manures which would complex Al^{3+} thus prevent its hydrolysis. It is the hydrolysis products of Al^{3+} that fix phosphorus in the soil solution. At half rates, the goat manure treatment (25 t/ha) and chicken manure treatment (15 t/ha) were the most effective in raising the soil pH. The chicken manure treatment raised the soil pH to 4.86 at half rate (15 t/ha) whilst the goat manure treatment at half rate (15 t/ha) raised the soil pH to 4.863. The results from the study were in line with the findings of Uwah & Enyo (2014), whom from their studies reported that goat manure was the most effective in raising soil pH. The pH levels are expected to increase with the addition of organic manures due to the release of ammonia from the decomposing manure (Hileman, 1972). Slight increase in soil pH were observed from the cattle manure at full rate (50 t/ha) treatment and the chicken manure at full rate (30 t/ha) treatment. Agyenim Boateng (2006) attributed this to probably the low ammonia content and buffer capacity of the manure. A slight decline in soil pH was observed from the control and the cattle manure treatment at half rate (25 t/ha). The pH from these treatments decreased the initial soil pH to 4.60 and 4.58. This can be attributed to that upon decay, organic manures release humic and fulvic acids which have the potential of lowering the soil pH.

4.2. Effect of Ameliorants on the Content of Heavy Metals in the Grain, Leaves and Stem

There were no significant differences ($P < 0.05$) in the content of heavy metals in the grain. This was in line with results by Nikoli & Matsi (2011), who stated that concentrations of all micronutrients in maize were not affected by fertilization. However, following manure application micronutrients' uptake by maize increased. The content of Zn was highest in the grain with the goat manure treatment at 50 t/ha (0.128 g/kg) and lowest in the chicken manure and lime treatments at half rate, 1.5 t/kg and 30 t/ha (0.025 and 0.021 g/kg). Though the Zn level was high in the goat manure treatment, it was within the recommended daily intake by WHO (1998). The daily intake for Zn by WHO standard is 0.005 – 0.182 g/kg Zn. Manganese was higher in the chicken manure treatments. This could have been attributed to the manganese content in the manure. The manure had the highest manganese content than the other manures (0.129%), while goat manure and cattle manure had 0.054% and 0.041% Mn respectively. At half rate the chicken manure treatment yielded 0.148 g/kg Mn, whilst at full rate the chicken manure treatment resulted in 0.139 g/kg Mn. The control treatment and the goat manure treatment at full rate gave the least content of Mn in the grain. The control treatment had 0.117 g/kg Mn while the goat manure treatment had 0.118 g/kg Mn. This was above the recommended daily intake for Mn (0.005g/kg). Adesoye et al., (2014) studied the heavy metal composition of manure of some domestic animals. The results showed that Zinc (Zn), Lead (Pb), Nickel (Ni) and Magnesium (Mg) were highest in layer chickens' manure. The high contents of these heavy metals in layer chickens' manure may have been associated with their addition to poultry feed for disease prevention and enhanced feed efficiency. Iron content was high in the control treatment and cattle manure treatment at half rate. The control treatment had 0.108 g/kg Fe in the grain while the cattle manure treatment at half rate had 0.101 g/kg Fe in the grain. This was within the daily recommended intake by WHO standard (0.004 – 0.212 g/kg). The Fe content in cattle manure was 1.57% and this explains the high Fe content in the grain. Results by Ahmad et al., (2009) indicated that amending soils with CM at the highest application rate provided the best crop performance in terms of root and shoot biomass, crop N, C, and other macro- and micro-nutrients.

In the control treatment, the high Fe content could have been a result of the addition of fertilisers during the plants' growing season. Cadmium was highest in the lime treatment at full rate, goat manure at full rate and both chicken manure treatments. All these treatments tallied in cadmium content and they all yielded 0.020 g/kg Cd in the grain. The lime treatment at half rate gave (0.015 g/kg Cd), the control, goat manure at half rate and cattle manure treatment at half rate gave the lowest quantities of Cd in the grain (0.017 g/kg).

The high Cd content in the grain resulting from the lime treatment maybe a result of high Cd in the liming material. The Cd content was higher in the grain than the daily intake limits set by WHO (0.00011 – 0.00076 g/kg). This suggests that the consumption of green maize with these levels of Cd may not be safe for human consumption as it is toxic to the human body. Manganese was also above the recommended WHO standards (0.005 g/kg) in the grain, leaves and stems in all the treatments.

Copper was highest in the control treatment (0.009 g/kg) and lowest in the chicken manure treatment at half rate, goat manure treatment at full rate and lime treatment at full rate. These treatments produced 0.003 g/kg Cu in the grain. The quantity of copper in the grain was within the daily recommended intake by WHO standard (0.0003 – 0.1075 g/kg). The low Cu content in the grain maybe due to complexation by a variety of organic molecules that may have had an affinity for copper ions. The low content of Cu in the materials used in the study may also explain the low content of this element in the grain.

Zinc was high in the leaves in plants grown on goat manure at full rate (50 t/ha) (0.128 g/kg). Iron was high in all the treatments. The control treatment pooled in Fe content in the leaves (0.305 g/kg Fe). The lime treatment at half rate (1.5 t/ha) and cattle manure treatment at full rate (50 t/ha) resulted in 0.214 and 0.202 g/kg Fe in the leaves. Manganese was highest in the leaves from the chicken manure treatment at half rate (15 000 kg/ha) (0.154 g/kg Mn). Cadmium was higher in both chicken manure treatments and lowest in the lime treatment at 3 t/ha. The chicken manure treatment at half rate yielded 0.002 g/kg Cd in the leaves, while the full rate treatment yielded 0.014 g/kg Cd in the leaves. This is not surprising because chicken manure contains high Cd content as well as other heavy metals. Similar results were obtained by Adesoye et al., (20014). High amounts of Cd were found in poultry manure from their studies. The lime treatment at full rate yielded 0.006 g/kg Cd in the leaves. The lime treatment, goat manure treatment and cattle manure treatment at full rate yielded higher quantities of Cu in the leaves. The treatments yielded 0.013, 0.013 and 0.012 g/kg Cu in the leaves. The maybe attributed to the partitioning of the elements controlled by biochemical process within the plants' system.

The lime treatment at full rate and cattle manure treatment at full rate were significantly similar and produced the highest levels of Zn in the stem, 0.084 and 0.034 g/kg respectively. Iron content in the stem was highest in the lime treatment at full rate (0.013 g/kg). This treatment was significantly similar to the control, cattle manure treatment at half rate, and goat manure treatment at full rate in Fe content in the stem. These treatments had Fe content of 0.140, 0.109 and 0.106 g/kg in the stem. Cadmium was highest in the chicken manure treatment at full rate and the treatment was significantly similar to the chicken manure treatment at half rate. At full rate, the amount of Cd in the stem was 1.002 g/kg and at half the rate Cd in the stem was 0.006 g/kg. The control treatment had the lowest quantity of Cd in the stem (0.002 g/kg). The chicken manure treatment and cattle manure treatment had the highest quantities of Mn in the stem (0.154 and 0.141) g/kg Mn. Copper was highest in the goat manure treatment, lime treatment and cattle manure treatment at full rate. The goat and lime treatments at full rate had 0.013 g/kg copper in the stem while the cattle manure treatment at full rate had 0.012 g/kg Cu in the stem. The lowest quantity of copper was obtained from the goat manure treatment at half rate (0.004 g/kg Cu) in the stem.

Cadmium and lead are the heavy metals of most concern because they may affect human health. Copper and zinc represent necessary micro-elements which could be harmful only if the concentration is too high. Additional variation in the concentration of metals in animal manures is associated with the age of the animal, type of ration, housing type and waste management practices. The type of bedding material in animal waste units may influence the litter's dry matter content and other chemical properties (Nicholson, 1999).

Application of livestock compost as a fertiliser helps to provide essential nutrients (K, Ca and Mg) to the plant but it can contaminate the environment with heavy metals; therefore, the heavy metal contents of manure must be exactly determined (Fardullah et al*.,* (2014). Besides the contamination of the soil for the trial with organic manure as sources for heavy metals, there are other possible sources of heavy metals which could have added to the contaminants. The site at which the trial was conducted is situated in an urban area and the experimental site was near sewage plant which is the main collector for domestic effluent around the area. In the experimental site, there is high industrialization taking place which could also contribute to the increase in the heavy metals content in the plant tissues. Atmospheric sources including burning of fossil, incineration of waste and industrial emissions could also be a possible source for high levels of heavy metals in the plant tissues. Biney et al*.,* (2011) states that, for most trace elements, anthropogenic emissions are more than equal to natural emission, the combustion of lead for example, is responsible for the widespread distribution of lead in the world.

Haung et al*.,* (2013) reported that the applications of different amendments decreased the amount of Pb and Zn in soils that was available for uptake by plants, but increased the availability of As. The results indicated that red mud, bone char and lime are potential amendments for modifying acidic soil contaminated by heavy metals. The study provided new potential materials for remediation of heavy metal contaminated soils (Haung *et al.,* 2013). A field experiment was carried out by Xiafung *et al.,* (2012) on the effects of the combined application of lime and superphosphate on growth and heavy metals (Cd, Pb, Zn, Cu) concentration of a low-accumulating cultivar of *Zea mays* in a soil contaminated by wastewater from a lead/zinc mining. The concentration of Pb in grain of Z*ea mays* increased with lime addition (Xiafung *et al.,* (2012). The concentrations of Cd, Pb, Zn and Cu in stem and leaf of *Zea mays* were all decreased by the single lime application and the lime and superphosphate mixed application and it was safe to be served as organic fertiliser. Probably these elements were converted to solids through reactions with lime.

5. Conclusion

The treatments were effective in increasing the soil pH. At full rate, the goat manure treatment (at 50 t/ha) and the lime treatment (at 3 t/ha) showed the highest influence on the soil pH. The goat manure treatment improved the soil pH from 4.77 to 5.14 whilst the lime treatment improved the soil pH to 5.13. At half rate, the goat manure treatment (25 00kg/ha) and chicken manure treatment (15 t/ha) were the most effective in raising the soil pH. The chicken manure treatment raised the soil pH to 4.86 at half rate (15 t/ha) whilst the goat manure treatment at half rate (15 t/ha) raised the soil pH to 4.863.

The content of Zn was highest in the grain with the goat manure treatment at 50 t/ha (0.128 g/kg) and lowest in the chicken manure and lime treatments at half rate, 1.5 t/kg and 30 t/ha (0.025 and 0.021 g/kg). Though the Zn level was high in the goat manure treatment, it was within the recommended daily intake recommended by WHO. The recommended daily intake for Zn by WHO is 0.0045 – 0.1819 g/kg Zn. Iron content was high in the control treatment and cattle manure treatment at half rate. The control treatment had 0.117 g/kg Fe in the grain while the cattle manure treatment at half rate had 0.101 g/kg Fe in the grain. This was within the daily recommended intake by WHO (0.004 – 0.212 g/kg). Cadmium was highest in the lime treatment at full rate, and both chicken manure treatments in the grain, leaves and stem. In the grain, these treatments yielded 0.022 g/kg Cd. In the leaves the lime treatment produced 0.009 g/kg Cd at half rate (1 500 kg/ha) whilst at full rate (3 t/ha) it produced 0.006 g/kg Cd. The chicken manure treatments (15 and 30 t/ha) produced 0.019 and 0.014 g/kg Cd. In the stem the chicken manure treatments (15 and 30 t/ha) produced 0.019 and 0.014 g/kg Cd respectively. This was higher than the daily recommended intake by WHO, which is 0.0001124 – 0.00076 g/kg. Copper was highest in the control treatment (0.009 g/kg) and lowest in the chicken manure treatment at half rate, goat manure treatment at full rate and lime treatment at full rate. These treatments produced 0.003 g/kg Cu in the grain. The quantity of copper in the grain was within the daily recommended intake by WHO (0.00025 – 0.1075 g/kg) in all the treatment. Zinc content was almost similar in all the different plant tissues, Cu was higher the in leaves and stem, and lower in the grain. Manganese, Fe, and Cd were higher in the grain and were equal in the leaves and stem.

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