COMPARISON OF THE PHYSICOCHEMIAL POTENTIAL OF BOILER ASH, POULTRY DROPPINGS AND INORGANIC FERTILIZER AND THEIR EFFECTS ON ULTISOL AND MAIZE PERFORMANCE IN SOUTH EASTERN NIGERIA

BY

EZEMA, RAYMOND ANIKWE PG/Ph.D/11/58321

DEPARTMENT OF SOIL SCIENCE UNIVERSITY OF NIGERIA, NSUKKA

NOVEMBER, 2016.

COMPARISON OF THE PHYSICOCHEMIAL POTENTIAL OF BOILER ASH, POULTRY DROPPINGS AND INORGANIC FERTILIZER AND THEIR EFFECTS ON ULTISOL AND MAIZE PERFORMANCE IN SOUTH EASTERN NIGERIA

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF DOCTOR OF PHILOSOPHY (PhD) IN SOIL SCIENCE

BY

EZEMA, RAYMOND ANIKWE

PG/Ph.D/11/58321

SUPERVISOR: PROF. C.L.A. ASADU

NOVEMBER 2016.

CERTIFICATION

This is to certify that EZEMA, RAYMOND ANIKWE a post graduate student in the Department of Soil Science with Registration No. PG/Ph.D/11/58321 has satisfactorily completed the requirements for research work for the degree of Doctor of Philosophy (Ph.D) in Soil Science (Environmental Pollution Management). The work embodied in this thesis is original and has not been submitted in part or full for any other diploma or degree of this or any other University.

Ezema , R. A.

(Student)

Prof. C.L.A. Asadu Supervisor

Prof. C.L.A. Asadu Head of Department

Date

Date

DEDICATION

I dedicate this work to my late son, Master Chijioke Franklin Ezema and late bosom friend, Mr. Anthony Nnaemeka Ibudialo.

ACKNOWLEDGEMENT

I thank the Almighty God whose blessings and grace have enabled me to accomplish this thesis successfully after about twenty years of unsuccessful attempt. It is my pride and privilege to express my sincere thanks and deep sense of gratitude to Prof. Charles A. Asadu, Head, Department of Soil Science, University of Nigeria Nsukka for his valuable advice and splendid supervision of this work. I would like to thank Dr. Godwin Nnaji of University of Abuja for his role at the commencement of this work.

I am highly indebted Profs. F.O.R, Akamigbo; M.E. Obi and Charles Igwe, Dr Peter Ezeaku (Internal Examinar), Dr.(Mrs) I.M.Uzo, Dr. S. E. Obalum and other lecturers of the Department of Soil Science, University of Nigeria, Nsukka for their encouragement and warm disposition.

My appreciation is also expressed to Mr. Cajethan Iwueze, Ngozi Nwosu, Austin, Martha, Anthony and other members of staff of the Department of Soil Science for their assistance. I would also wish to thank Engr. Daniye of National Space Research and Development Agency - Centre for Basic Space Science Nsukka for assisting me in the procurement of meteorological data of the area of study.

I am highly indebted to the staff of Department of Agricultural Technology, Enugu State Polytechnic, Iwollo especially Miss Chukwu Chikaodili and Miss Onyejekwe Mmasinachi for their roles in accomplishing this task.

The author wishes to express his thanks to the staff of Solive Vegetable Mills Ltd Nsukka who provided invaluable cooperation and guidance during the collection of the boiler ash used for this study.

Finally, I wish to express my love and gratitude to my family, especially my wife Emmanuela Nkechi Ezema, my son Emmanuel Uchenna Ezema and Timothy Chigozie Ugwoke for their continuous support, encouragement and understanding extended to me in the course of the study.

Ezema, Raymond Anikwe.

TABLE OF CONTENT

Title	Page
Title page	i
Certification	ii
Dedication	iii
Acknowledgement	iv
Table of content	v
List of tables	xi
List of Figures	XV
Abstract	xvi
CHAPTER ONE: INTRODUCTION	1
CHAPTER TWO: LITERATURE REVIEW	3
2.1. Boiler Ash Generation	3
2.2. Ash Disposal Strategies	4
2.3. Physico-Chemical and Mineralogical Properties of Boiler Ash.	6
2.3.1. Physical Properties of Boiler Ash	7
2.3.2. Chemical and Mineralogical Properties of Ashes	8
2:4. Application Rate and Combinations	11
2.5. Fertilizing Value of Boiler Ash, Crop Growth and Yield	15
2.6. Effect on Seed Germination and Seedling Establishment	17
 2.7. Integrated use of boiler ash with organic and inorganic materials as fertilizer and soil amendment 2.8 Effect of Boiler Ash on Uptake of Nutrients and Toxic Elements by 	18
Crops and Environmental Quality	20
2.9.0. Soil Response to Boiler Ash Application	23
2.9.1. Effect of boiler Ash on Soil Physical Properties	23
2.9.1.1. Effect of boiler ash on soil texture	23
2.9.1.2. Effect of boiler ash on soil bulk density	24
2.9.1.3. Effect of boiler ash on pore size distribution and aggregate stability	25

2.9.1.4. Effect of boiler ash on soil hydraulic conductivity	26
2.9.1.5. Effect of boiler ash on rheological properties of soil.	26
2.9.1.6. Effect of boiler ash on soil water retention	27
2.9.1.7. Effect of boiler ash on soil electrical conductivity.	28
2.9.1.8. Effect of boiler ash on soil erosion	29
2.9.2. Effect of Boiler Ash on Soil Chemical Properties.	30
2.9.2.1. Effect of boiler ash on soil pH	30
2.9.2.2. Effect on soil nutrient status.	32
2.2.10. Effect of boiler ash on soil biological properties.	34
CHAPTER THREE: MATERIALS AND METHODS	37
3.1. Site Description	37
3.1.1. Location	37
3.1.2. Climate	37
3.1.3. Agriculture and Vegetation	37
3.1.4. Geology	38
3 .1.5. Soils	38
3.2. Materials Used	38
3.3. Soil Sampling and Storage	38
3.4. Boiler Ash Sampling	39
3.5. Determination of Physical Properties of Boiler Ash, Poultry Manure and Soil Samples	39
3.5.1. Determination of particles size analysis of boiler ash	39
3. 5.2 Determination of particles size distribution	39
3.5.3. Determination of bulk density of soil	39

3.5.4 Determination of bulk density of boiler ash and poultry droppings	40
3.5.5 Determination of saturation moisture percentage of soil, boiler ash and poultry droppings	40
3.5.6 Determination of saturated hydraulic conductivity and permeability of soil	40
3.5.7 Determination of total and air porosity of soil	41
3. 5.8 Separation of water-stable aggregates of soil	41
3.6. Determination of Chemical Properties of Boiler Ash, Poultry Manure, Soil and Maize Grain Samples.	42
3.6.1 Determination of organic carbon and organic matter	42
3.6.2. Determination of total nitrogen	42
3.6.3. Determination of pH	43
3.6.4. Determination of available phosphorus	43
3.6.5. Determination of soil exchangeable bases and cation exchange capacity (CEC)	43
3.6.6. Determination of soil exchangeable acidity (Al ³⁺ + H ⁺)	43
3.6.7. Determination of base saturation.	43
3.6.8. Determination of electrical conductivity (EC)	43
3.6.9 Determination of exchangeable sodium percentage (ESP) and sodium absorption ratio (SAR)	43
3.7. Land Preparation	44
3.8. Experimental Design and Treatments	44
3.9. Application of Soil Amendments	46
3.10. Planting	46
3.11. Cultural Practices	46
3.12. Data Collection	46
3.12.1. Measurement of Growth Characteristics	46
3.12.1.1. Germination percentage	46

3.12.1.2. Plant height	46
3.12.1.3. Stem diameter (cm)	47
3.12.1.4. Number of leaves per plant	47
3.12.1.5. Leaf area index (LAI)	47
3.12.1.6. Shoot biomass (dry matter) yield per plant (g)	47
3.12.2. Measurement of Yield and Yield Components	48
3.12.2.1. Fresh cob weight (g)	48
3.12.2.2. Grain yield /plot	48
3.12.2.3 .Weight of 100 seeds (g)	49
3.12.2.4. Harvest index	48
3.12.2.5. Sustainable yield index (SYI) and Agronomic efficiency (A E)	49
3.12.2.6. Percentage yield reduction (YR)	49
Statistical analysis	50
CHAPTER FOUR: RESULTS AND DISCUSSION	52
4.1. Physico-Chemical Properties of the Soil Prior to Treatment Application.	52
4.1.1. Soil physical properties prior to treatment application.	52
4.1.2. Soil chemical properties prior to treatment application.	54
4.2. Metrological Data of the Experimental Site	56
4.3. Agronomic potentials of the Boiler Ash and Poultry droppings	60
4.3.1. Physical properties of the boiler ash and poultry droppings	60
4.3.2. Chemical properties of the boiler ash and poultry droppings	62
4.3.3. Micronutrient and Heavy Metal Concentrations in the Boiler ash and Poultr droppings	у 65
4.4. Treatment Effects on Soil Physical Properties	71

4.4.1. Particle size distribution	71
4.4.2 Bulk Density and Porosity	73
4.4.3. Soil Water Characteristics	76
4.4.4. Saturated Hydraulic Conductivity	78
4.4.5. Aggregate Size Distribution	79
4.4.6. Soil Aggregate Stability	82
4.4.7. Electrical Conductivity	85
4.5. Treatment Effects on Soil Chemical Properties	87
4.5.1. Soil pH	87
4.5.2. Organic Carbon and Total Nitrogen	89
4.5.3. Available Phosphorus (P)	91
4.5.4 Concentration of Sulphur	93
4.5.5 Exchangeable Bases (Ca, Mg, K, Na).	94
4.5.6. Cation Exchange Capacity (C.E.C) and Percent Base Saturation.	96
4.5.7. Mobile Aluminum and Hydrolytic Acidity.	98
4.5.8 Percent Exchangeable Sodium and Sodium Adsorption ratio.	99
4.6 Content of Boron, Cadmium, Manganese, Zinc and Copper.in soil	102
4.7.0. Treatment Effects on Crop Performance	104
4.7.1 Maize germination.	104
4.7.2. Maize Height	106
4.7.3. Maize Stem Diameter	109
4.7.4. Maize Leaf Number per plant.	112
4.7.5. Maize Leaf Area Index	115
4.676. Number of Days to 50 % Maize Tasselling and Silking	118
4.7.7. Maize Dry Shoot Biomass	120
478 Maize Growth Rate Estimates	124

4.8. Maize Grain Yield and Yield Components.	127
4.8.1. Average Maize Cob Weight per Plant.	127
4.8.2. Maize Grain Yield (tha ⁻¹)	127
4.8.3. Harvest Index of Maize	130
4.8.4. 100 seed weight of maize	132
4.8.5. Sustainable Yield Index (SYI) and Agronomic Efficiency (AE) of Maize	132
4.8.6. Concentration of Nutrients in Maize-Grains	134
4.8.7. Maize Grain Concentration of Heavy Metals	137
4.8.8. Metal Bio concentration Factor (BCF)	141
49. Correlation of Soil Properties with Maize Yield Parameters	143
4.9.1.Soil Physical Properties and Maize Biomass and Grain Yields	143
4.9.2. Soil Chemical Properties and Maize Biomass and Grain Yields	145
4.9.3.Soil Physical Properties and Nutrient and Heavy Metal Concentrations in Maize Grains.	147
4.9.4.Soil Chemical Properties and Nutrient and Heavy Metal Concentration in Maize Grains.	149
4.9.5. Maize Growth and Yield Traits.	151
CHAPTER FIVE: SUMMARY AND CONCLUSION	
REFERENCES	157
APPENDICES	185

х

LIST OF TABLES

Table 1: Treatments applied, their designations and application rates	45
Table 2: Theoretical analysis of variance (ANOVA) Table for the analysis of the data collected	51
Table 3: Initial soil physical properties of the study location	53
Table 4: Initial soil chemical properties of the study location	55
Table 5: Particle size, Saturation Moisture Content (S.M.C) and Bulk density of the boiler ash	61
Table 6: Chemical properties of boiler ash and poultry manure	63
Table 7: Micronutrient and heavy metal content of the boiler ash and poultry manure	66
Table 8: Particle size distributions as influenced by different rates and combination of the soil amendments	72
Table 9: Soil bulk density and porosity as influenced by different rates and combinations of boiler ash, poultry manure and NPK 20:10:10	74
Table 10: Soil water retention and saturated hydraulic conductivity as influenced by different rates and combinations of boiler ash, poultry manure and NPK 20:10:10	76
Table 11: Soil aggregate size distribution as influenced by different rates and combination of boiler ash, poultry manure and NPK 20:10:10 during the first cropping season	80
Table 12: Soil aggregate size distribution as influenced by different rates and combination of boiler ash, poultry manure and NPK 20:10:10 during the second cropping season	81
Table 13: Effect of different rates and combinations of boiler ash, poultry manure and NPK 20:10:10 on soil aggregate stability as evaluated using different aggregation indices	83
Table 14: Impact of different rates of boiler ash, poultry manure NPK 20:10:10 and their admixtures on soil electrical conductivity.	86
Table 15: Impact of different rates of boiler ash, poultry manure NPK 20:10:10 and their admixtures on soil pH	88
Table 16: Impact of different rates of boiler ash poultry manure, N.P.K 20:10:10 and their admixtures on soil organic matter and nitrogen composition	90

Table 17: Impact of different rates of boiler ash, poultry manure, NPK 20:10:10 and their admixtures on soil phosphorus and sulphur contents	92
Table 18: Impact of different rates of boiler ash, poultry manure NPK 20:10:10and their admixture on soil exchangeable cations.	95
Table 19: Impact of different rates of boiler ash, poultry manure, NPK 20:10:10 and their combinations on soil heavy metal content	97
Table 20:_Impact of different rates of boiler ash, poultry manure, NPK 20:10:10 and their admixtures on soil cation exchange capacity and percent base saturation	100
Table 21: Impact of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on soil mobile aluminum and hydrolytic acidity	101
Table 22: Effect of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on Exchangeable Sodium Percentage and Sodium Adsorption Ratio	103
Table 23: Mean effect of different rate of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on germination % and relative germination of maize seed	105
Table 24: Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on maize plant height at 4, 6, 8 and 10 weeks after planting (WAP) during the first cropping season	107
Table 25: Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on maize, plant height at 4, 6, 8 and 10 weeks after planting (WAP) during the second cropping season	108
Table 26: Mean effects of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on maize stem diameter (cm) at 4, 6, 8 and 10 weeks after planting during the first planting season	110
Table 27: Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on maize stem diameter at 4, 6, 8 and 10 weeks after planting (WAP) during the second cropping season	111
Table 28: Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on maize leaf number at 4, 6, 8 and 10 weeks after planting (WAP) during the first cropping season	113
Table 29: Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on maize leaf number at 4, 6, 8 and 10 weeks after planting (WAP) during the second cropping season	114

Table 30: Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on maize leaf area index at 4,6,8, and 10 weeks after planting (WAP) during the first cropping season	116
Table 31: Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on maize leaf area index at 4,6,8, and 10 weeks after planting (WAP) during the second cropping season	117
Table 32: Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on number of days to 50% tasselling and silking	119
Table 33: Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10: 10 and their combinations on maize dry shoot biomass (g plant ⁻¹) at 4,8, and 12 weeks after planting (WAP) during the first cropping season	121
Table 34: Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on maize dry shoot biomass (g/plant) at 4,8, and 12 weeks after planting (WAP) during the second cropping season	122
Table 35: Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on maize growth rate and relative growth rate during the first cropping season	125
Table 36_Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on maize plant growth rate and relative growth rate during the second cropping season	126
Table 37: Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on maize cob yield (g cob ⁻¹) and maize grain yield (tha ⁻¹)	128
Table 38: Effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on 100-seed weight and harvest index of maize	131
Table 39: Sustainable yield index (SYI) and agronomic efficiency (AE) of maize grown in soil amended with different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations	133
Table 40: Effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on nutrient composition of maize grains during the first cropping season	135
Table 41: Effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combination on maize grain nutrient composition of during the second cropping season	136
Table 42: Effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on heavy metal concentration in maize grains during the first cropping season.	138

Table 43: Effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on heavy metal concentration in maize grains during the second cropping season	139
Table 44: Bio-concentration factor (BCF) of heavy metals in maize grains as affected by different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations.	142
Table 45: Correlation coefficient matrix between soil physical properties; and maize biomass and grain yields	144
Table 46: Correlation coefficient between maize biomass yield, grain yield and soil chemical properties	146
Table 47: Correlation coefficient between grain concentrations of nutrients, heavy metals and soil physical properties	148
Table 48: Correlation coefficient between grain concentrations of nutrients, heavy metals and soil chemical properties	150
Table 49: Correlation Values among the Growth and Yield Traits measured in this study	152

LIST OF FIGURES

Figure 1: Mean monthly rainfall (mm) of the experimental site during the period of cropping	57
Figure 2: Mean monthly air temperature (°C) of the experimental site during the period of cropping	58
Figure 3: Mean monthly relative humidity (%) of the experimental site during the period of cropping	59

ABSTRACT

The power boiler ashes (BA) from burnt oil- palm mill wastes at Solive Vegetable Oil Mills Ltd, Nsukka has not been assessed for its crop-use potentials before, and its disposal could pose environmental challenge in future. Several studies have shown that recycling such ash through agronomic production system could alleviate the risks associated with its disposal and make it a value-added input in crop production with the potentials of solving the challenges posed by high cost of mineral fertilizers and low fertility status of soils. The use of this BA can only be sustained if soil quality improvement and increased crop productivity effects can be demonstrated. The extent to which it can improve an Ultisol and increase maize performance relative to commonly used organic manure (poultry droppings) and inorganic fertilizer (N P K fertilizer) is not known. This study compared the crop-use potentials of BA with that of poultry droppings (PM), inorganic fertilizer and their combinations as well as their effects on an Ultisol and maize performance. It also compared the effectiveness of the different levels of BA, PM, and NPK fertilizer and their combinations on soil boron, cadmium and zinc loadings and uptake by maize plant. The study was conducted on an Ultisol at the Research Farm of the Department of Soil Science, University of Nigeria, Nsukka. The experiment was laid out in a randomized complete block design with three replications. The treatments were a control (no amendment), and a sole application of three levels of BA (10, 50, and 100 t ha⁻¹) designated BA₁₀, BA₅₀ and BA₁₀₀, respectively; three levels of PM (5, 10, and 20 t ha⁻¹) designated PM₅, PM₁₀ and PM₂₀, respectively; three levels of NPK 20-10-10 fertilizer (75, 150, 300kg ha⁻¹) designated NPK₇₅, NPK₁₅₀ and NPK₃₀₀, respectively. In addition, combinations of different levels of BA with different levels of each of PM and NPK fertilizer (BA100+PM5, BA50+PM10, BA10+PM20, BA100 +NPK75, BA₅₀ +NPK₁₅₀ and BA₁₀ +NPK₃₀₀) were studied. The plots were planted with Oba Super II maize variety and changes in the physicochemical properties of the soil and crop-use potentials of the amendments were monitored for two consecutive years and compared. The physcico-chemical properties of the BA, PM and soil were determined pre and post experiment. Maize grain yield parameters were measured. Data collected were subjected to one-way analysis of variance and significant treatment means were separated by Fisherøs least significant difference at 5% level of probability. The BA consisted mostly of sand-sized particles (741 g kg⁻¹), and had low bulk density (0.37 Mgm⁻³), high saturation moisture content (77%), high pH (8.9) and high electrical conductivity (441 d S cm⁻¹). The contents of organic carbon was high (12.5 mg kg⁻¹), nitrogen very low (0.24 mg kg⁻¹) content, phosphorus high (298.5 mg kg⁻¹) and K high (9.58 cmolkg⁻¹) while, Fe, B, Cd and Pb values were relatively low. The PM had a higher bulk density (0.49 Mg m⁻³), N (4.15 mg kg⁻¹) and Fe (167.0 mg kg⁻¹) but lower in P (8.32 mg kg⁻¹) than BA. The NPK plant nutrient ratios of the BA, PM and NPK mineral fertilizer were 1-147-5, 25-5-1, 20-10-10, respectively. Application of \times 50 t ha⁻¹ BA increased significantly the sandósized particles resulting in pseudo-change of soil texture from sandy clay loam to sandy loam. The bulk density of the control soil (1.92 Mg m⁻³) was significantly reduced to 1.76, 1.03 and 0.88 Mgm⁻³ in NPK₃₀₀, BA₁₀₀ and BA₁₀₀+PM₅ treated plots, respectively. Total porosity (61%) and water holding capacity (54%) were highest in the BA₁₀₀ treated plots. The BA₅₀ + NPK₁₅₀ treated plots had the highest mean weight diameter of 0.69 and 0.76 at first and second cropping seasons

respectively. The BA100 + NPK75 treated plots had the highest saturated hydraulic conductivity (141cm⁻³ hr⁻¹) at the second cropping season. The highest soil pH value (7.7) was obtained in plots treated with BA₅₀ and BA₁₀+PM₂₀. The BA₁₀₀ + PM₅ plots had the highest soil N (0.16 mg kg⁻¹) and residual available P (124.6 mg kg⁻¹). The highest soil exchangeable K (0.56 cmolkg⁻¹) and Mg (17.8 cmolkg⁻¹) were obtained from BA₁₀₀+NPK₇₅ treated plots. The NPK₃₀₀ treated soil had the highest concentration of boron (4.56 mg kg⁻¹) and sodium adsorption ratio (0.37) whereas Cd concentration (0.8mg kg⁻¹) was highest in BA₅₀ treated plots. The BA₁₀₀ treated plots had the highest Mn concentration of 11.6 mg kg⁻¹ and Zn (12.04 mg kg⁻¹). Application of BA_{100} impeded maize germination (21%) but its residual effect on germination was highest (83%). The dry shoot biomass at 12 weeks after planting (WAP) was highest (421 g plant⁻¹) in $BA_{50} + PM_{10}$ treated plots. Application of $BA_{10} + PM_{20}$ produced tallest maize plants (89.5 cm plant⁻¹), highest leaf area index (7.32) and had the maximum maize grain yield of 5.43 tha⁻¹ at the first cropping season; while, PM_{20} produced the highest residual effect (2.56 tha⁻¹). The nitrogen (2.3 mg kg⁻¹) and potassium (96.1 mg kg⁻¹) concentrations in maize grain from plots treated with BA_{100} and BA_{100} + NPK₇₅, respectively, were the highest. Residual effect of PM₅ produced grains with the highest P content (0.82 mg kg⁻¹). The boron (14.5 mg kg⁻¹) and Cd (4.53 mg kg⁻¹) concentrations were highest in maize grains grown in BA₁₀₀ + NPK₇₅ and BA₅₀ + PM₁₀ treated plots, respectively. The bio - concentration factor of the heavy metals in maize grains as affected by the amendments were in the order B > Zn > Cd while their residual effects were Cd > Zn > B. The result revealed that BA when compared with other alternatives (PM and NPK fertilizer) was superior in soil conditioning but poor as a source of plant nutrient. Therefore, BA should not be applied alone without supplementary nutrient source especially when used for crop production. It is also preferable to blend it with organic manures like poultry droppings rather than inorganic manure such as NPK.

CHAPTER ONE

INTRODUCTION

The use of biomass wastes as fuel for power boilers to produce steam or electricity is important for reducing dependence on fossil fuel and cutting greenhouse emissions and other pollutants. Such practice generates a residue known as boiler ash which contains the bulk of the mineral fraction of the original biomass (Khan and Quasim, 2008; James *et al.*, 2012). Given the global focus on waste recycling and bioenergy development, the use of biomass wastes in energy generation has been on the increase and as a result, the production of boiler ash has continued to increase.

The disposal of the ash represents an emergent environmental challenge in many developing countries as these wastes are deposited on soil surfaces without any criteria supported by scientific and environmental concern. Such practice covers several hectares of valuable land and pollutes the soil, air and water, which ultimately affect human health (Pathak et al. 1996; Finkelman et al. 2000; Borm, 1997; Pujari and Dash, 2006). According to Singh and Gupta (2014), a suitable and sustainable solution for the disposal of boiler ash is required to be done to minimize the threat to the environment. An agricultural utilization of these ashes could alleviate the risks associated with its disposal and make it a value-added product of agriculture with the potentials of solving the challenges posed by high cost of mineral fertilizers and low fertility status of soils. However, there are many restrictions to agricultural utilization of these materials. Non-judicious application of boiler ash to soil can deteriorate soil quality as well as crop growth (Shukla et al. 2003; Sharma and Kalra, 2006). The heavy metals in boiler ash may be toxic to plants and animals; the high salt content may induce salt stress in plants; the pH value in soil may affect the mobility of elements and the leaching of heavy metals into ground water could be of environmental concern (Glardano et al. 1983). It also leads to deterioration of soil structure, water intake capacity of the soil and alteration of electrical conductivity and chemical properties such as pH, C.E.C. etc. These changes in the soil can affect the moisture availability, seedling emergence and crop establishment, root and shoot growth and consequently crop yield.

Boiler ash from sugarcane bagasse has been used as soil amendment in China, India, Pakistan, America etc. to improve crop yield and soil physico-chemical characteristics in an environmentally friendly manner (Khan and Qasim, 2008). So far, published data on the physical, chemical and agronomic properties of boiler ash from Nigerian bio-energy plants are somewhat limited. Most reported works have dealt with ashes generated at low temperatures as farm sanitation measures and applied at low rates (Ayeni *et al.*, 2008; Onwuka, 2009; Ojeniyi *et al.*, 2010). The results of these studies may not accurately predict, the potential uses and safety of boiler ash from burnt oil palm mill wastes and applied to an Ultisol for maize production in southeastern Nigeria.

The use of boiler ash from oil palm mill wastes in agronomic production system can only be sustained if soil quality improvement and increased crop productivity effects can be demonstrated. Most local farmers are unaware of the nutrient imbalance of boiler ash (Heraldsen *et al.*; 2011) and equate it with commonly used poultry manure or NPK fertilizer while, most researchers on boiler ash use in agriculture recognized the nutrient imbalance. They corrected the imbalance either by applying basal doses of NPK fertilizer (Khan and Qasim. 2008), or integrating it with other nutrient sources (Karmakar et al., 2009, Mohammadi and Rokhzadi. 2012); the results of which may not be used to accurately predict the potentials and safety of boiler ash applied without blending with other nutrient sources. Therefore, there is a research gap between farmers practice and the research focus especially with respect to boiler ash (BA) from oil palm mill wastes. The extent to which this BA can improve soil quality and increase maize performance relative to commonly used organic manure (poultry droppings) and inorganic fertilizer (N P K fertilizer) is not well known. This study compared the crop-use potentials of BA, poultry droppings (PM), inorganic fertilizer (NPK, 20-10-10) and their combinations as well as their effects on the properties of an Ultisol and maize performance in order to identify possible constraints associated with BA use for crop production. This is for developing a utilization strategy for boiler ash that would maximize their beneficial effects while minimizing any potential for negative effect on soil and environmental quality.

The specific objectives were to:

- (i) compare crop-use potentials of BA derived from burning oil palm mill wastes with that of PM and NPK fertilizer,
- (ii) determine the BA application rate that would have minimal environmental impact while still providing benefit to soil health and maize performance,
- (iii) evaluate and compare the effects of different levels of BA, PM and NPK fertilizer in an Ultisol, growth and yield of maize, and
- (iv) assess the comparative effectiveness of the different levels of BA, PM, and NPK fertilizer and their combinations on soil boron, cadmium and zinc loadings and uptake by maize plant.

CHAPTER TWO

LITERATURE REVIEW

2.1. Boiler Ash Generation

Demirbas *et al.* (2009) observed that with industrialization, it is expected that the future generation of electricity will be from direct combustion of residues and wastes obtained from biomass. Biomass boilers are one medium for efficiently combusting the biomass and obtaining its energy. Many combusting technologies such as fixed bed, fluidized bed, and pulverized bed combustion are available. Fluidized bed combustion is the best technology to burn a fuel with low quality, high ash content and low calorific value (Saidur *et al.* 2010) and also because of their ability to handle different fuels, flexibility, low operating temperature and low emission (Sandberg *et al.*, 2011). During the burning process, the organic component of the biomass is burned off quickly, whereas the incombustible materials undergoes partial melting and tends to fuse together to form ash (Huang, 1990).

The formation of the ash takes place in the furnace of the boiler. They include bottom ash, fly ash, boiler slag, flue gas desulfurization (FGD), gypsum and other power plant products (American Coal Ash Association, 2008). It consists of a wide range of elements (Quaak *et al.*, 1999). In wood, ash represents less than 2% while in agricultural crop materials it can be 5-10% and up to 30-40% in rice husks and milfoil. Because of high ash content that is present in biomass, boiler combustion processes are known to produce large amounts of ash (James, 2012). Patnaik (1992) observed that there is a thumb rule for every megawatt of power, one acre of land is required for disposal of ash accumulating to a height of 8-10m in ash pond.

It is estimated that the sugar industry in Pakistan is producing about 2.0 million tons of boiler ash every year (Nasir and Qureshi, 1999). In India, fly ash generation from 82 utility thermal power plants was around 125 million tons by 2003-2004 and is likely to touch 155 million tons in 2020 (Singh and Kumar, 1997). In the USA, up to a total of 111 million metric tons of these products were produced of which fly ash 64.3, bottom ash 25.5, boiler slag 2.0, and FGD gypsum 28.5 million metric tons (US Geological Survey, 2006). In 2007, the total had increased to 131 million metric tons (American Coal Ash Association Educational Foundation, 2010). In China, about 375 million tons of coal ash (fly ash and bottom ash) was produced in 2009 (Green peace, 2010). In Nigeria, biomass-based power plants currently account for about 54% of installed capacity of utilities and projections by the Nigerian Energy Commission indicate that coal will fuel the power sector for at least the next

three decades (Sambo, 2008). The total amount of ash produced in Nigeria is not known and difficult to determine. This may be due to lack of understanding and information about all biomass sources and their net contribution to boiler ash production processes. As the demand for bio-energy production increases, the ash and residue volumes will increase. This has significant implications for waste management and handling.

2.2. Ash Disposal Strategies

Waste management and utilization strategies are major concern in many countries. Companies with wood or biomass burning facilities are looking for alternative and more sustainable methods of waste disposal with minimum environmental impacts. Land application is considered one alternative (Campbell, 1990; Khan and Qasim, 2008) as it has the potentials to protect human and the environment by reducing contaminant bio-availability and mobility at a considerable lower cost than other available options (EPA, 2007). In addition, it has both soil amending and nutrient enriching properties that is helpful in improving crop growth and yield in low fertility acid soils (Shoennan and Van Deventer, 2000). However, the recycling of the boiler ash onto agricultural land provides a challenge to the producers and end-users who both have, duty of careøto ensure the method of disposal is managed in a sustainable way. Careful management means that soil and water resources are not contaminated; the agricultural production system remains stable and a land use alternative remains available to future generations (Barry *et al. 1999*).

Wood ashes produced through incineration of wood by home owners or by farmers during clearing of forested land or during farm sanitation are disposed of by incorporation during soil site preparation for agricultural production. However, the disposal of boiler ash produced through thermo chemical degradation of biomass-based products is one of the major problems of developing countries. The disposal absorbs huge amounts of water and, energy, and cultivable land areas are occupied by ash ponds (Basu *et al.*; 2009, Kishor, 2010). Traditionally, industrially produced wood ash has been disposed of in large landfills or stored in disposal ponds within the mills (Appendix. Land filling is not an optimal solution for disposal because of landfill space limitations and tipping costs (Daniels *et al.*, 2002). The alkaline character and high concentration of minerals substances in fly ash have resulted in attempts at using it as fertilizer or amendment to enhance the physico-chemical properties of soil (Kishor *et al.*, 2010).

The best management strategy for waste ashes is recycling and re-using (Lam et al, 2010) although the ashes contains high concentrations of heavy metals, salts, chloride and

organic pollutants. The utilization of ash allows industry to implement the 3R principle of the reduction, reuse and recycling of materials as beneficial products (Yoshida *et al.*, 2007).

Gutierrez *et al.* (1993) reported that the assessment of physical characteristics, chemical composition and leaching behaviors of a waste fly ash (from a coal-fired power station) should be performed prior to selection of fly ash management method. In addition, Patterson (2001) noted that factors to be considered when developing land application programs involving wood ash are:

- i. What are the characteristics of the ash being proposed for land application?
- ii. What are the characteristics of the surrounding agricultural soil and would they be suitable for ash application? Should laboratory analysis of initial soil samples indicate high pH, EC or SAR these soils would be unsuitable for ash application.
- iii. What are the short and long term environmental consequences of boiler ash application? Single high application rates are often evaluated to determine rates at which toxicity symptoms may occur. However, there is need to study the effects of multiple applications on soil chemistry and crop production.
- iv. Are there current guidelines pertaining to the application of boiler ash to agricultural soils?
- v. What are the alternatives to boiler ash? Is there a cheaper alternative to wood ash that provides similar benefits?
- vi. Who would benefit economically from the application of boiler ash? Economically, both generators and end users of boiler ash benefit from its use.
- vii. Who benefits environmentally from the land application of wood ash? Agricultural, Industrial, and Community partners would all benefit environmentally from the land application.
- viii. Would the farmers and local communities accept and support the land application of boiler ash?

Birtschi (2000) also outlined the various parameters that are of concern when using wood ash in a land application programs. These include soil pH, electrical conductivity (EC), hot water soluble boron (B_{Hws}), cadmium (Cd), Zinc (Zn) and accumulation by plant tissue of B, Cd, and Zn. They also noted that sodium adsorption ratio (SAR) was not significantly affected by ash application. Soil pH, EC, B_{Hws} , Cd and Zn play a significant role in determining sustainable agronomic rate for the application of wood ash, and may influence restrictions imposed in the future due to the accumulation within the soil.

The application of waste to soil as a recycling option can only be sustained if there are demonstrate able ecological benefits. They are usually justified in terms of elevated organic carbon and its effect on soil conditions and stimulations of microbial activity and nutrient supply. It is sustainable only if threshold level of pollutants does not exceed tolerable limit (Kumar, 2004). Wood ashes when applied properly reduce exposure pathways and immobilize contaminants to limit their bio-availability (USPA, 2007). The addition of amendments restores soil quality by balancing pH, adding organic matter, increasing water holding capacity, re-establishing microbial communities and alleviating compactions.

Management strategies for integrated use need to be evolved. The ultimate aim is to optimize crop production, maximize returns, minimize the depletion of soil nutrients and minimize nutrient losses or negative impact on the environment (Roy *et al.*, 2006). Inference drawn from studies on fly ash application in agriculture suffer from the variation of ash characteristics, soil types and agro-climatic conditions; therefore correlating the effect of ash between various plant species and soil type is difficult (Ram *et al.*, 2011). Lima *et al.* (2008) therefore concluded that each fly ash type need to be studied separately owing to profound dissimilarity amongst all ash types. There is a dearth of information on the soil recycling option of large volumes of ash residues arising from oil palm mills.

2.3. Physico-Chemical and Mineralogical Properties of Boiler Ash.

The appropriateness of boiler ash as soil amendment is related to its mineralogical, physical and chemical properties (Tsadilas, 2014). Therefore, knowledge of their composition is a first step in assessing their effects on agricultural lands. The information on ash properties has been reported in the literature by many authors (Campbell, 1990; Kalra *et al.*, 1997; Aigbodion *et al.* 2010; Das *et al.* 2013 etc). It has been emphasized by most of these authors that boiler ash has quite variable physical and chemical properties. They attributed these differences to different types of fuel (species of wood and the amount of bark), furnace temperature, duration of combustion period, priming method, efficiency of weathering (aging) before final disposal. This makes it difficult to draw conclusions from other researchers apply only to the ash samples tested by those researchers and must not be taken as absolutes. However, the variations within the same plant are quite predictable provided that fuel source and plant operations remain the same (Meyers *et al.*, 1996). In other words, laboratory and field data of properties of ash from a given source are valid as long as the plants operating parameters do not change.

2.3.1. Physical Properties of Boiler Ash

The physical properties of ashes that ensure selection of the most suitable way for ash utilization are particle size distribution, moisture content, bulk density, compressive strength, permeability and porosity (Esuden *et al.*, 1999). Boiler ash is produced in different forms such as bottom ash; fly ash etc. Due to the differences in the formation of these ashes, they have distinctly different physical appearance.

Anderson (1978) reported that bottom ash is composed of hard and angular to subangular particles with shiny black color or smooth surface texture much like crushed glass. Fly ash on the other hand is composed of very fine particles with an average diameter < 0.10mm, which are aggregated into spherical particles of 0.01-100 mm sizes which are hollow spheres (cenospheres), filled with smaller amorphous particles or crystals (pelospheres) (Davison *et al.*; 1979, Sadasivan *et al.*; 1993). Aigbodion *et al.* (2010) reported that an SEM/EDAX analysis of bagasse ash obtained from Zango area of Zaria in Kaduna state of Nigeria reveals the presence of prismatic, spherical and fibrous structure and can withstand a temperature of up to 1600° C with a density of $1.95g/cm^{3}$.

Particle shape and surface texture significantly affect the frictional characteristics of material (Ram *et al.*, 2011). Angularity contributes to particle-interlock and rough surface textures inhibit movement of one particle on another. They noted that these components create interesting properties in fly ash such as very large specific surface area ranging from 2500 to 4000 cm²g⁻¹ and consequently high sorption capacity which make fly ash suitable as sorbent for flue gas clearing from sulphur components, N0₃x, gaseous organic and for removal from waste water of several toxic metal ions.

Coal fly ash is heterogeneous and has varying particle sizes, moisture retention, high water holding capacity, low to intermediate bulk density, non-magnetic and magnetic components (Khandkar *et al.*, 1993; Sarkar *et al.*, 2005). Mean particle density for non-magnetic and magnetic particles is 2.7 and 3.4gcm⁻³ respectively (Natusch and Wallace, 1974); while, the moisture retention ranges from 6.1% at 15bar to 13.4% at $^{1}/_{3}$ bar. Etiegni *et al.* (1991) studied wood ash structure and its change during wetting. They suggested that ash is essentially hydrophilic with particle swelling through absorption of water into the pores by capillary action simultaneously with chemical change through hydration of oxides to form new compounds. After four weeks of wetting, expansion had increased the volume by 12.5% on the original. This effect they noted could be beneficial and detrimental in soil where ash might be used as an amendment. In clay soil, small pores might easily be clogged by wetted

ash, causing decreased aeration but in sandy, free draining soils, this water holding capacity could be very beneficial to plant growth.

Dolar-Mantuan (1978) reported that ashes with high ion content have corresponding high specific gravities and water absorption that vary considerably depending on the porosity and surface texture of the ash. Campbell (1990) also noted that ash has a small particle size and low density. Density varies with the carbon content, the greater the carbon content, the lower the density of the ash.

Indian fly ashes have low bulk density, high water holding capacity and porosity, rich silt-sized particles, alkaline nature, negligible solubility and reasonable plant nutrients (Ram *et al.*; 2011). On the other hand, Das *et al.* (2013) stated that the physical properties of fly ash used in their experiment composed of 61.3% sand, 10.4% silt and 26.29% clay particles with a textural class of sandy clay loam. It has a dry bulk density of 0.57gcm particle density of 0.98gcm⁻³, porosity of 3.0%, water holding capacity of 78.2% and volume expansion of 30.34%. Ayininuola and Olasebikan (2013) reported that the basic physical property of rich husk ash are specific gravity 1.63 and bulk density 588.54Mgm³

In general, fly ash has low bulk density (1.01-1.43gcm⁻³), hydraulic conductivity and specific gravity (1.5-1.4gcm⁻³) (Roy *et al.*,1981;Mattigod *et al.*,1990).From the review, there is dearth of information on physical properties of boiler ash especially those derived from burning oil based crop wastes.

2.3.2. Chemical and Mineralogical Properties of Ashes

Knowledge of properties of ashes, mainly chemical ensures selections of the most appropriate way for its utilization. The chemical characteristics can be divided into alkalinity, macro and micro elements (Demeyer *et al.*, 2001). Chang (1998) noted that the chemical properties of ash that influence their utilization include chemical composition, loss on ignition, heavy metal and leach ability, organic constituents and chloride content.

Huang (1990) reported that the composition of ash material is controlled primarily by the source of the coal and not by the type of the furnace. On the contrary, Ayuso *et al.* (2006) stated that the enrichment of nutrients and metals in fly ashes are dependent on combustion temperature. At a combustion temperature of between 800 and 1200 °c most elements vaporize. In addition to elements volatilization characteristics, element retention through condensation process determines the fate of the volatilizable elements. Misra *et al.* (1993) noted that the mass of K, S, B and Cu decrease with the burning temperature but this is less

definite for Na and Zn. The mass of Mg, P, Mn, Al, Fe, and Si do not change with temperature relative to Ca, which is assumed constant.

Boiler ash is typically low in nitrogen, sulphur and sometimes phosphorus but consists of salts, oxides and hydroxides of Ca, Mg, Na and K (Lerner and Utzinger, 1986) and trace amounts of metals (Etiegini *et al.*, 1991). The P content in woody biomass ash is usually low, whereas the P content in ash based on cereals and oil seed crops or animal manure is higher (Eichler-lobermann *et al.*, 2008).

Lam (2010) reported that CaO is the most abundant compound that exists in fly ash, which constitutes up to 46% but SiO₂ is the most abundant compound that exists in bottom ash containing up to 49%. Generally, the heavy metal content in fly ash is higher than bottom ash due to the vaporization of metals during combustion and the process of metal adsorption on the surface of fly ash particles. Fly ash contains much higher chloride content than bottom ash. This may be attributed to the lime scrubber in the air pollution control system which removes acidic gases such as HCl, thus resulting in a high amount of chloride content remaining in fly ash after the air pollution system. Diebel *et al.* (1992) indicated that the type of poly aromatic hydrocarbon (PAHS) found in wood ash are those of the two or three ring constituents which are less toxic than the four and five ring compounds.

Fly ash has significantly alkaline nature with a pH ranging from 4.5 to 12.0 depending on the S-content of parental coal, high ionic content and electrical conductivity and low levels of nitrogen and phosphorous (Rautaray *et al.*; 2003, Tiwari *et al.*;2008, Anusari *et al.*,2011). They noted that in addition, fly ash contains a high concentration of toxic heavy metals such as Cu, Zn, Cd, Pb, Ni, and Cr etc. which along with low nitrogen and phosphorous coupled with low organic content, mark it as a nutritive deficient substrate. However, the total concentration of heavy metals is quite different from the extractable or available concentration (Campbell, 1990). Sharma *et al.* (2012) reported that occurrence of micronutrients like Cu, Zn, Fe, in high enormity makes it apposite to use as manure to argument crop productivity. Also, aluminum in fly ash is mostly bound in insoluble aluminosilicate structures which considerably limit its biological toxicity (Page *et al.*, 1979).

The calcium carbonate equivalent (CCE) of wood ash reported, ranges from 13.2 and 92.4% calculated on 180 different wood-fired boiler ash samples (Vance, 1996). The capacity of ashes as a liming agent to neutralize soil acidity and act as a soil amendment agent depends on the Ca and Mg concentration and the sum of P+K concentration (Nurmesniemi *et al.*, 2011).

Yunusa *et al.* (2009) examined the differences between fly ash obtained from burning semi-bituminous (black) coal and lignite (brown) coal. The ash from the semi-bituminous coal was grey in color, while that from the brown was reddish. Both ashes were strongly alkaline and the red ash were strongly saline with an EC (1:5water) of 19:1 dsm⁻¹ compared to 0.51 for the grey ash. The high salinity (1:5water) of the ash was mainly due to its high soluble salt content while the red color reflected its high concentration of Fe₂0₃. The concentration of trace metals and cations were generally higher in the red ash than in the grey ash. Other elements such as Cd, Mn and Pb were up to three times higher in the red ash than in the grey ash.

Page *et al.* (1979) and Jamil *et al.* (2004) investigated the chemical composition of bagasse ash. The results showed that bagasse ash was devoid of N, with high pH value (9.2). It contained sufficient P (110 ppm) and K (210 ppm) and abundant micronutrient like in Zn (65ppm), Cu (55ppm) Fe (267ppm) and Mn (194ppm). Schiemenz *et al.* (2011) observed that the highest P contents (10.5%) were measured in cereal ash and lowest in straw ash (1% P). however, the solubility of P in water was low but about 80% of P was soluble in citric acid.

Wood ashes derived from burning of twigs and branches of apple (*Malus domestica*, *Borkh*) and spruces (*Picca Spp*) in furnace contained 0.06 mg kg⁻¹ N, <1mgkg⁻¹ total P, K⁺ (59156 mg kg¹) Na⁺ (1333 mg kg⁻¹), Zn (437 mg kg⁻¹) and a pH of 12.8 (Boh *et al.*, 2013). Ayeni *et al.* (2008) observed that ash obtained from burning cocoa pod husk as a method of farm sanitation had 6.5% OC, 0.5% N, C: N 12, Fe (1.22 mg kg⁻¹) Zn (0.13 mg kg⁻¹), Cu (0.33 mg kg⁻¹) and Mn (1.22 mg kg¹). Otuloge *et al.* (2012) reported that the main constituents of palm kernel shell ash (PKSA) are silicon as SiO₂, aluminum (as AlO₃) and iron oxide as (Fe₂O₃). The total amount of SiO₂, Al₂O₃ and Fe₂O₃ present in PKSA is 66.57%.

Agbede and Adekiya (2012) observed that the chemical composition of ash collected from a bakery consist of N (1.72 %), pH of 11.1. While, Soretire and Olayinka (2013) reported that the wood ash used in their study was strongly alkaline in reaction (11.3) low in organic carbon content (8.8kg⁻¹), available P (26.98 mg kg⁻¹) total N (0.9 kg-1) and high in Ca²⁺, Mg²⁺, K⁺ and Na⁻ with values of 4.56, 2.83, 4.1 and 1.7 cmol kg-1 respectively.

The mineralogy of ash is important to its utilization or disposal. Ash reactivity during utilization results in interaction between the crystalline and glassy phases that make up the ash and the matrix into which it is placed. For disposal, it is the mineralogy of the ash and its water reacted products that controls the release rate of potentially harmful trace elements (Mc Carthy *et al.*, 1987). The main constituent is silica (SiO₂), ferric oxide (Fe₂O₃) and alumina (Al₂O₃). Though these constituents are reported as oxides, they occur in ash as a mixture of

silicate, oxides and sulphates with small quantities of phosphates and there compounds (Albernethy *et al.* 1969).

An X-ray diffraction (XRD) analysis of powdered sample of ash was carried out by Nurmesniemi *et al.* (2011) to determine the mineral composition of bottom and fly ashes obtained from incineration of peat and wood residues. The XRD spectra show that both contained silicate minerals such as microcline (KALS1O₂O₈) and quartz (SiO₂). Muscovite (KAL₂Si₃O₁₀) (F.OH)₂ and anorthrite (Ca Al₂Si₂O8) which are silicate minerals only existed in bottom ash whereas oxide minerals such as Calcium aluminum oxide (CaAl₂O₄), Srebrodolskite (Ca₂Fe₂O₅) and lime (CaO) as well as anhydrite (CaSO₄) which is a sulphate mineral only existed in fly ash.

The mineral composition of mixtures of bottom ash and fly ash from a grate-fired boiler contained a sulphate mineral 6 enttringite (Ca₆Al₂(SO₄)₃ (OH)₁₂ (H₂O)₂₆, carbonate minerals - quartz (SiO₂), Calcite (CaCO₃) and silicate mineral - rhodonite (Mn, Fe, Mg, Ca)₅ (SiO₃)₅ and hydrooxylapatite (Ca₄ (Po₄) ₃ (OH, F, Cl)₃ which is a phosphate mineral, as well as oxide minerals such as marokite (Ca CMn₂O₄) and periclase (Mg0). Also, in a study of chemically and physically characterize bagasse ash, Aigbodion *et al* (2010) observed that the XRD analysis of the ash reveals quartz (SiO₂), Cliftonite (C), Moissanite (SiC) and Titanium oxide (TiO) as primary compounds.

Literature inferences on the chemical and mineralogical properties of boiler ash indicate a wide difference in ashes obtained from different plant species and burning conditions. Therefore, the chemical properties of ashes obtained from incinerating agricultural wastes like cocoa pod husk, rice husk cannot be accurately used to predict the chemical properties of boiler ash obtained from burning oil palm mill wastes in boilers.

2.4. Application Rate and Combinations

Problems in BA use as a soil amendment occur when it results in undesirable change in soil pH, imbalance in nutrient supply, boron toxicity in plants, excess supply of sulphate and potentially toxic trace elements (PTEs). These problems, however, are usually associated with excess or inappropriate BA applications. In agronomic utilization of boiler ash, there is a challenge to appropriately tailor the quantities of nutrients contained in the waste with the crop need. There has been a lack of definitive recommendation in terms of application rates needed for achieving optimum plant yield (Yunusa *et al.*, 2008). Agronomic application rates are suggested to avoid potential detrimental effects posed by increase in soil pH, salinity, excess micronutrients (Vest *et al.*, 1999) and avoid the nutrient immobilization effects that are frequently reported when utilizing carbon rich soil amendments (Miller and Rahe, 1998). NSWEPA (1997) suggested the use of soil contaminant concentrations and likely N requirements of a crop to determine the application rate of boiler ash. However, there is difficulty in estimating the mineralisation rates of N and P from the often-large reserves of organic materials, into forms available to plants. Precise information is not available on rates of mineralisation of nutrients from boiler ash. Since these ashes are equivalent to low-grade fertilisers, quite often-high application rates are used with little consideration given to crop nutrient needs. Therefore, any benefits in recycling boiler ash may be offset by environmental degradation if excessive applications of nutrients occur. Furthermore, soil contamination may result from heavy metals or persistent toxic organics, some or all of which can occur in these materials.

Nnabude (1995) observed that the ability of soil amendments to effect significant changes in certain soil physical properties depends on the rate of application. Such physical properties as bulk density, total and macro porosity, aggregate stability (WSA) and plastic limit require application rates of burnt rice mill waste of 37.5 Mg ha⁻¹ to undergo significant changes capable of reconditioning the soil for improved productivity. Relatively high loading rates (>100 ton/acre) of ash are required to significantly influence soil physical properties such as water holding capacity and aggregation (Jones and Amos, 1976). However, fly ash is added to soils primarily to affect chemical properties such as pH and fertility, and loading rates are limited by chemical effects in the treated soil (Daniels *et al.*, 2002). Naylor and Schmidt (1986) reported that extractable P, K, and Ca and pH of soil amended with ash were linearly related to the rate of ash application.

Patterson (2001) reported that soil pH, electrical conductivity, hot water soluble boron, cadmium and zinc play a significant role in determining sustainable agronomic rates for application of wood ash and may influence restrictions imposed in the future due to accumulation within the soil. The study revealed that wood ash applications of <25 tha⁻¹ increased pH and available levels of B, K, S and Zn while decreasing available levels of Fe in Luvisolic soil. Minimal difference was observed in both soil pH and available nutrient levels between 12.5 and 25tha⁻¹ application rates. The result suggested that minimal benefit would be observed in the short term (i.e. 3years) when applying ash at rate greater than 12.5tha-1. Therefore, agronomic applications (<50 tha-1) of wood ash can have positive effects on soil properties.

Boiler ash with high soluble salts may cause problems with seed germination and plant establishment (Kalra *et al.*, 1997). Timing of the ash application plays a significant role

in avoiding problems of high soluble salt on seed germination. Ash used as soil amendment should be applied as far in advance of plant establishment as possible to allow time for the salts to leach out of the root zone (Magdoff *et al.* 1984; Koreak, 1996). They noted that ash absorbs herbicides and pesticides and could cause concentrated alkaline conditions before neutralization by the soil. Magdoff also recommended that because of ash variability, the calcium carbonate equivalent should be measured routinely.

Use of weathered ash can also alleviate problems of soluble salts. Martens and Beahm (1976) reported that the use of ash at rates of 58 tons/acre was successful while fresh fly ash caused salt related problems at 29 tons/acre. Fresh fly ash was also reported to be more toxic to dauphine magna than stabilized ash and both ashes showed highest toxicity at the beginning of the sampling period (Krakow, 2010).

Brod (2011) suggested the determination of application rate of ash by calculating with respect to the amount of total K content (extraction with 7 HNO₃) set to be equal of the plant uptake of divalent cations such as Ca^{2+} or Mg^{2+} (Manitoba, 2013).

Mittra *et al.* (2003) reported that there was beneficial effect of repeated application of fly ash as compared to one time application at the same level. According to Norwegian Ministry of Agriculture (2003) bottom wood ash is usually on class 1 considering the content of heavy metals in the materials. Therefore, their use on agricultural land would be restricted to 40tons dry matter of material per ha in 10 years.

Gray and Rock (1988) simulated the effect of precipitation on the leaching of ash components after large application. A loamy soil and a silt loam soil were mixed with wood ash at a loading rate of 27 metric tons/ha and then water at pH of 5.6 was added to the column at a rate of 90cm³/day. The study concluded that ash could be applied to the loamy sand at 12 metric ton/acre but should be applied at a lower rate on the silt loam. Also, Steponkus (1992) reported that ash application of 27tons/ha did not result in violation of the ground water regulation.

Khan and Quasim (2008) applied boiler ash as organic fertilizer at 3, 12,25,50,125 and 250 tha¹ along with basal dose of NPK at 120, 90, and 60kg ha⁻¹ respectively at the time of sowing in form of urea, K_2SO_4 and triple super phosphate. By comparing the levels of bagasse ash application, 50tha⁻¹ was found to be the optimal dose regarding important growth, yield and yield components of wheat crop in pots, as well as in the field experiments.

Research by Etiegni (1991) evaluated wood ash at low and high application rates as an agricultural soil supplement and liming material in a greenhouse study. Wheat and polar were grown on six Idaho soils amended with different ash concentrations (0, 40, 80, 160, 320, and 640 metric tons/ha. No detrimental effects were observed at ash levels equal to or lower than 40 metric tons/ha.

Yeledhalli *et al.* (2007) evaluated the effect of different levels of fly ash (0, 25, 50, 75 and 100 tons/ha) with or without recommended chemical fertilizer rate on physico-chemical, biochemical and biological properties of alfisols, the yield parameters of sun flower, soil enzymes, dehydrogenase, urease and alkaline phosphatase. The seed yield in control plot was 521 kgha¹, which increased significantly to a maximum of 1194kgha⁻¹ at 25t ha⁻¹ fly ash in non-fertilized plots and 1182kgha⁻¹ at 50tha⁻¹ fly ash in NPK amended plot. There was decline in the urease activity due to higher doses of fly ash application with NPK. This was attributed to pozzolanic effect of fly ash, which reduced air capacity of the soil.

Ezema *et al.* (2013) studied the effects of boiler ash application rates of 0, 3, 10, 25 and 50 tha⁻¹ under zero and conventional tillage systems on soil chemical properties, growth and yield of pepper. The 25tha⁻¹ rate was considered the best rate to improve pepper yield, soil chemical characteristic and provide a reasonable economic means to recycle the waste.

Jena *et al.* (2013) studied the effect of soil/fly ash (FA) combinations on maize growth and yield (50% soil +50% FA,70% soil +30% FA, 70% soil + 20% FA + 10% cow dung and soil + chemical fertilizer. The percentage increases of harvested crop over control plot was 21%, 31%,41% and 42% for 50% soil +50% FA, 70% soil + 30% FA, 70% soil + 20% FA + 10% cow dung and soil + mineral fertilizer respectively. They concluded that 70% soil + 20% FA + 10% cow dung was the ideal application rate as it showed good performance in production compared to control and reduces the amount of cost in comparison to the fertilizer plot.

Adejei-Nsiah and Obeng (2013) reported that the highest fruit yield of garden egg (9.52 tha¹) was obtained at palm bunch application rate of 4tha¹ while for the pepper and okra, highest fruit yields of 6 and 4.98 tha⁻¹ were obtained at PBA application rate of 2tha⁻¹

Yunusa *et al.* (2009) observed significant reduction in relative chlorophyll concentrations in Canola (Brasica napus) only when alkaline fly ash was added to soil at rates exceeding 125Mgha⁻¹. Also, in a Terrestrial Plant Growth Test (Guideline 2008) protocols of the Organization for Economic Cooperation and Development (OECD), Yunusa et al (2009) observed that at moderate application rates (Ö 10 Mgha⁻¹) of semi-bituminous (gray ash) and lignite (red ash) both ashes increased (P< 0.05) growth rates and concentrations of chlorophyll a and b, but reduced carotenoid concentrations. Growth rates and final dry weights were reduced for all of the six test species when additions rates exceeded 10 Mgha⁻¹ for gray ash and 5 Mgha⁻¹ for red ash.

Swedish Forest Agency set the upper limit on the total amount of ash added to the forest to avoid unwanted effect as no more than 3 tons DS per hectare during a 10-year period and no more than 6 per hectare during a life cycle of the forest (Krakow, 2010).

The effect of boiler ash application rate (0, 896, 1792 Mtha⁻¹) with a liming equivalent of 20% and a pH of 11.6 on Slash pine (Pinus elliotti(L)) tree growth, moisture retention, plant nutrient and metal uptake and biomass accumulation, were studied under both field and green house conditions. Plant mortality was monitored in the field plots consisting of similar ash application rates with application methods, surface and sub-surface with incorporation. Tree mortality was higher in the surface treatment where there was no buffer between newly planted tree roots and ash in the field. High application rates of ash reduced above ground biomass in the unfertilized plots by 40% and addition of fertilizer decreased the reduction to 15%. Therefore, boiler ash may be successfully used as a soil amendment in forest soils when applied at agronomic rates (below 60 Mtha⁻¹) (Vest *et al.*, 1999).

In this study, the choice of application rates was aimed to confine treatments to rates that would be within the range of agronomic practice when applying soil amendment and the rate for disposal option without causing damage to the Soil. Also, full and fractional levels of recommended application rates of poultry droppings and NPK 20:10:10 were included to draw a comparison with different level of boiler ash. In addition, integrated levels of boiler ash and poultry droppings or NPK fertilizer were also included.

2.5. Fertilizing Value of Boiler Ash and Effect on Crop Growth and Yield.

The application of boiler ash as a fertilizer has brought about several studies aimed at evaluating the fertilizing capacity of these products. Thus, field, screen house and greenhouse experiments have been considered. Brown *et al.*(1997) have indicated through their studies that fly ashes contain numerous compounds such as calcite (CaCO₃), anhydrite CaSO₄, and dolomite [Ca Mg(CO₃)₂] that have the potential to be a nutrient source and a soil amendment for the reclamation of acid and sodic soils. It is evident that the confirmed enrichment of the soil due to ash application would cause changes in the metabolic and physiological activity of plants (Saarasalmi *et al.*, 2001; Arvidisson and Lundkvist, 2003) and thus may manifest in crop yield.

Crop response to fly ash application may vary widely from beneficial to toxic depending on the concentrations of various elements present in it (Grewal *et al.*, 2001; Kalra *et al.*, 2000). Differences among plant species are often associated with the plants tolerance of trace elements (Adriano *et al.*, 1980); Airken and Bell, 1985); which may manifest in the

responses of their photosynthetic pigment concentrations. Trace elements such as Cu, Mn, Pb, and Zn readily displace Mg from the chlorophyll molecules (Kupper *et al.*, 1998) and plants differ in the way they adapt to elemental stress. Yunusa *et al.* (2009) concluded that plant dry weights, rather than concentrations/ or instantaneous rates of photosynthesis are more consistent for assessing subsequent growth in plants supplied with fly ash.

As a whole, results on growth, yield and yield parameters have been generally positive. Khan and Qasim (2008) showed that most yield parameters of wheat improve in response to the favorable effect of boiler ash on soil characteristics. The same effect has been observed with a variety of crops: alfalfa, sorghum (Sorghum bicolor) and field corn (Furr *et al.* 1978), maize ((Adeji-Nsiah, 2012, Bob *et al.*, 2013); cassava (Ojeniyi *et al.*, 2009); pepper (Ezema *et al.*, 2013) Indian mustard (Gautain *et al.*, 2002); Guava (Swain and Padhi, 2012) and cocoa seedling (Akanbi *et al.*, 2013). Fly ash amendment also improved the performance of oil seed crops such as sunflower (Helianthus sp), sesame (Sesamum indicum), turnip (Brassica rapa) and groundnut (Arachis hypogea (Jala and Goyal, 2006); Inam (2007). Thetwar et al ;(2006).Medicinal plants such as cornmit (Mentha arvensis) and vertiver (vetiver zizanoides) were also successfully planted in fly-ash mixed with 20% farm yard manure and mycorrhiza (Sharma *et al.*, 2001).

Occasionally, the application of ashes does not always induce positive response. Biomass ash may reduce the growth of crops due to high salt content and as such have negative impact on growth factors such as nutrient uptake and assimilation (Huang *et al.*, 1992; Spark, 1996). It also has negative effect on soil active herbicide (Miller and Rahe, 1988; Muller-warrant *et al.*, 1991); which are frequently a part of local farm management practice. On the basis of their studies, Singh *et al.* (2008) have reported that Beta vulgaris L. var All Green H plant is sensitive to fly ash concentrations and they suggested that fly ash should not be used as an amendment for leafy vegetables like B. Vulgaris.

The observed discrepancies between different studies may be ascribed to differences in abiotic factors such as soil type, different degrees of stabilization and dosage used (Aronsson and Ekelund, 2004; Ram *et al.*, 2007). They suggested the development of suitable mathematical models for judicious combination of ash dose, soil conditions and selectivity of plant species along with co-application of inorganic and readily oxidizable organic substrates.

Naylor and Schmidt (1986) equated wood ash fertilization effect to commercial fertilizers on the basis of the N, P (P_2O_5) and K (K_2O) concentrations for a commercial wood stove (low temperature burn) the ash has a high proportion of K and would be equivalent to a

0-3-4 fertilizer. They noted that the availability of K was a linear function of the amount added.

Ohno (1992) reported reduced rates of phosphorus availability in wood ash due to its low solubility and uptake by maize plants in eight different soils. Schiemenz and Eichlerlobermann (2010) observed that plants have different potentials to utilize P from ashes. The exudation of ions, organic acids or enzymes into the rhizosphere enables crops to acquire P from ashes from less available fractions

Grain yield is a function of the interaction among various yield components that were affected differentially by the growing conditions and crop management practices. It is an important factor in determining the fertility and productivity of a certain soil especially in cereal crops (Jamil and Qasim, 2008). In this study, no attempt was made to separate the liming effect from the nutrient value of the amendments.

2.6. Effect on Seed Germination and Seedling Establishment.

Germination and crop stand establishment are prime plant growth processes which play a major role in deciding subsequent growth and yield and have been evaluated under varying levels of ash incorporation within the soil. Kalra *et al.*, (1997) observed that fly ash incorporation delays germination of crops most likely because of increased impendence offered by the soil/ash matrix to germinating seeds. This causes reduced growth of crops in the earlier stages, which subsequently may lead to reduced yield under unfavorable environment. Differential responses of crops to ash matrix in soil were noted, rice and maize been less sensitive than wheat, chickpea and lentil.

Application of boiler ash increases soil salinity, electrical conductivity and chromium concentration (Kumar, 2002; Jouybari, 2012). Basalah (2010) observed that salinity decreases both the rate and percentage of germination and emergence in different crops. The decrease was attributed to the combined effect of osmotic pressure and toxicity of salts (Al-moaikal, 2006) or due to the effect of added chloride ions (Gill *et al.*, 2002). Maas and Nieman (1978) observed that in addition to toxic effects of certain ions, higher concentration of salt reduces the water potential in the soil medium, which hinders water absorption by germinating seeds and thus reduces germination. While, Ayaz *et al.* (2000) noted that a decrease in germination because of salinity appeared to be induced by disturbances of metallic process leading to increase in phenolic compounds. In a study to determine and

compare the inhibitory effects of chromium on seed germination and early seedling growth of melon (Cucumis mello .L.), Akinci and Akinci (2010) observed that excess chromium (10mgl⁻¹ and above) limited germination rate, germination index, mean germination time and germination uniformity index values in germination level. Response of seedlings to chromium was more than that of seed germination. This evident was based on the impermeability of seed coat and selectivity of embryos against chromium.

Swain and Padhi (2012) revealed that significantly higher germination of guava seeds was recorded in 25:75 coal ash and soil media which was statistically at par with 50:50 coal ash and soil. The study indicated that the germination percentage decreased with increase in coal ash concentration in the media. Increase in germination over the control was attributed to higher moisture in the 25:75 coal ash and soil composition.

Yunusa *et al.* (2009) observed that fly ash addition had no significant effect on germination of barley, rye grass, canola, radish, field pea and lucerine, noting that germination depends on seed storage reserve. In addition, Singh *et al.* (2011) reported no inhibitory effect of fly ash on seed germination except at 100% fly ash. The observation was in line with that of Karpate and Choudhary, (1997) on wheat; Sharma *et al.* (2001) on maize and rice; Anusari *et al.* (2011) on S. melongena and S. oleracea. They noted that the possible reason for this may be the role of growth regulators and the balance between promoters and inhibitors; which shifts due to the trace element.

2.7. Integrated use of boiler ash with organic and inorganic materials as fertilizer and soil amendment.

Nitrogen, phosphorus and potassium ratios in waste materials usually are unbalanced in comparison to the plants need (Heraldsen *et al.*; 2011) Combining various waste resources could be a possibility to overcome the challenge of unbalanced NPK ratios in waste materials. Several studies have been carried out on the use of boiler ash along with mineral fertilizer and organic materials in an integrated manner. The result obtained indicated that these mixtures are more efficient than the separate applications. Thus, Agbede and Adekiya (2012) using a mean of 3 years study, observed that relative to control, 5tha⁻¹ poultry droppings (PM) + 5tha⁻¹ wood ash (WA) increased pod yield of okra by 255% as against 23% by 5tha⁻¹ WA alone and 64% PM alone. The superior performance of the combined application was adduced to increased availability of nutrients following the addition of faster decomposing and nutrient releasing poultry droppings.
Karmakar *et al.*(2009) observed an increase in growth, yield and yield attributes of rice (up to 110 and 23 percent) over control and mineral fertilizer (CF) respectively under integrated use of paper factory sludge (PFS) or Farmyard manure (FYM) as organic source, fly ash (FA), rice husk ash (RHA) or lime as soil amendment and mineral fertilizer. In addition, the uptake of N, P, K, Ca, Mg, Mn, Zn, Cu, and Co increased under the integrated plant nutrient system. A marginal increase in content of heavy metals viz., Se, Cd, and Ni in the plant tissue was also noted, although all these remained below the safe limit. In rice-based cropping system, uptake of N, P, K, Ca, Mg, S, Fe, Mn, Zn, and Cu by subsequent mustard crop was higher under the residual fertility of 10tha⁻¹ fly ash + 5tha⁻¹ paddy straw + mineral fertilizer or 10tha⁻¹ fly ash + 2.5tha⁻¹ green manure + mineral fertilizer as compared to chemical fertilizer or fly ash alone (Rautarary *et al.* 2003).

Inam (2007) applied different basal doses of fly ash at 0, 5, 10, and 15 tha⁻¹ along with two doses of nitrogen (40 and 20 kg ha⁻¹). Uniform basal dose of 30 kg ha⁻¹ and 40 kg ha⁻¹ was also applied. In general, fly ash at 10tha⁻¹ with 20 kg ha⁻¹ N proved better while higher doses proved deleterious.

Mittra et al. (2003) attempted to develop an integrated plant nutrition system (IPNS) utilizing fly ash (FA) and paper factory sludge (PFS), along with farmyard manure (FYM), crop residue (CR) and mineral fertilizer for rice-peanut cropping system. Direct and residual effects of fly ash were assessed based on crop response and changes in soil characteristics. Application of FA at 10 tha⁻¹ in combination with organic sources (PFS/FYM/CR) and CF increased the grain yield of rice, pod yield of peanut and equivalent yield of both crops by 31, 24 and 26 percent respectively as compared to C.F alone. The yield advantage derived by peanut through IPNS was greater than rice. Moreover, there was saving of C.F in order of 64% N, 44% P₂O₅, and 43.3% K₂O. It also increased the availability of P, K, Ca, Mg, Zn, Cu, and Co besides improving soil physicochemical properties.

Brod (2011) tested the effects of four N-rich waste resources meat and bone meal (MBM), composted fish sludge and two industrial compost (Dynea 2009 and Dynea 2004) alone, and in combination with K-rich bottom wood ash on Italian ryegrass (*Loluim multifilorum*). Mineral fertilizer treatments resulted in the highest yield being significantly different from all waste combination. Potassium fertilization effect of BWA was hidden by sufficient K supply from the soil but K-Al values of soils that were fertilized with BWA were significantly higher than soil of unfertilized control treatments. Min N + BWA treatment had poor establishment due to local pH increase and initial P deficiency but leaching or denitrification of NO_3^{-N} was avoided so that the treatments still resulted in vigorous growth

towards the end of the season. On the other hand, Pradham *et al.* (2010) reported that the combination of human urine and wood ash in field experiment on red beet (*Beta vulgaris*) resulted in greater production than mineral fertilizers. Haraldsen and Krogstad (2011) also reported that BWA has potential P and K fertilization effects.

Mohammadi and Rokhadi (2012) reported that combined application of farmyard manure, compost, chemical fertilizers and fly ash elevated the nitrogen uptake rate and grain oil yield in chickpea and sunflower. However, EPA (2007) asserted that if pH of wood ash is >8.3, it can drive off nitrogen from manures or biosolids and decrease nutrient value. In addition, if blended with manure and seeded immediately, the ammonia generated can kill the seed. Use of swine manure with fly ash balanced the ratio between monovalent and bivalent cations Na⁺ + K⁺/ Ca²⁺ + Mg²⁺, which are detrimental to the soil and thereby increased the availability of Ca and Mg (Giardini, 1991).

Abudlraheem (2012) in a study reported that the performance of sorghum and nutrient availability could be significantly increased by combining reduced levels of urea and sawdust ash (SDA). Combination of 1.5tha⁻¹ of SDA + urea increased soil OM, N, P, K, Ca tissue K and Mg. The use of SDA reduced need for inorganic fertilizer in sorghum cultivation. Papadimitrion *et al* (2008) asserted that the combined use of fly ash and sewage sludge result in low photo toxicity. In addition, co-application of readily oxidizable organic substrate could prohibit B-induced inhibition of microbial respiration (Page *et al.*, 1979).

Babadele and Ojeniyi (2013) observed that combination of 4tha⁻¹ sawdust +10tha⁻¹ slam weed (Chromolaena odorata + 300kgha⁻¹ NPK fertilizer showed highest values of the measured parameters on cassava at 3, 6,9 and 12 months after planting (MAP). At 12 MAP its root count was higher by 109% compared with 400kg NPK fertilizer.

Soretire and Olaynika (2013) reported that cow dung applied at 5tha⁻¹ in combination with 2.5tha⁻¹ wood ash significantly (P<0.05) increased grain yield of soybean. The grain yield increased over the control with 11% at Epe and 58% at Ijebu waterside. According to Kuchanwar *et al.* (1997) application of 10tha⁻¹ fly ash and 25:50:0 NPK resulted in better growth and yield attributes which led to the highest pod yield of groundnut.

2.8. Effect of Boiler Ash on Uptake of Nutrients and Toxic Elements by Crops and Environmental Quality.

Heavy metals play an important role in the environment. Some are physiologically essential at low concentrations for plants and/or animals (Cu and Zn) while others are

potential pollutants (As, Cd, Pb and Hg), due to their toxicity and environmental persistence (Shaver *et al.* 1985). These elements are either potentially toxic at high concentration within the soil or at risk of bioaccumulation within plant and animal tissues and cadmium is probably the worst of these elements (Aronsson and Ekelund, 2004; Singh and Gupta, 2014).

Boiler ash is characterized by high alkalinity and salinity as well as high content of toxic trace elements (Tripathy and Sahu, 1997). There is an increasing tendency to favour land application over other means of disposal because, they have characteristics potentially beneficial for agriculture (the 'beneficial use' philosophy) despite the fact they may have other properties undesirable for agriculture or may contain significant concentrations of these elements.

Little is known about the mechanism of mobilization, uptake and transport of most environmentally hazardous heavy metals such as Pb, Cd, Zn, Sr, and Cu (Raskin *et al.*, 1997). They noted that a large proportion of these metals remain sorbed to solid soil constituents. To acquire these õsoil bound metals, phyto-extracting plants have to mobilize them into the soil solution through secretion of metal-chelating molecules into the rhizosphere to chelate/solubilize õsoil boundö metal. It can also be accomplished through root reduction of soil bound toxic metals by acidifying their soil environment with protons extruded from the roots and finally roots can employ rhizospheric organisms (mycorhizal fungi or root colonizing bacteria to increase the bio-availability of metals.

Determination of the total concentration of these elements (metalloids) is not sufficient to assess the environmental impacts, since their specific chemical forms dictate their mobility, availability and toxicity (Huang *et al.*, 2007; Jamali *et al.*, 2009). Germination tests, biometric measurements and chemical analysis (Lau *et al.*, 2001) can be used to evaluate the toxic action of boiler ash on crops. The relative root elongation and germination index were observed to be more sensitive indicators of toxicity than seed germination in thermal power station ash amended soils (Zucconi *et al.*, 1981; Teaca and Bodirlau (2008). They noted that seeds of cereals provide a suitable systems for a wide range of toxicological assays applicable to the estimation of risks to the environment, ecosystem and in some cases vertebrates/human.

Manitoba (2013) noted that usually seeds contain lower concentrations of most trace elements than the vegetative parts. Therefore, the part of the plant harvested is important to consider in soils that have high concentrations of trace elements. In the study performed to observe the influence of fly ash amendments on growth and accretion of heavy metals in pea plants (Sharma *et al.*,2011) reported that translocation factor revealed that toxic heavy metals

like Cd, Ni and Pd are retained in the below ground while micronutrients like Cu, Zn and Fe are trans-located to above ground parts. Cha *et al.*(1999) observed that addition of alkaline fly ash (pH >9.0) may in addition to amplifying the availability of trace metals, increase SO_4^- and other nutrients but nitrogen.

A literature search by Mitchell and Black (1997) found no published reports of environmental, crop production or crop quality problem provided the ash was applied as alternative to an agricultural liming material. At higher application rate of ash, toxicity symptoms have been observed however, these rates are too high to be considered for agricultural use (Etiegni *et al.*, 1991).

Sharma and Kalra (2006) reported that application of un-weathered fly ash may have a tendency to accumulate elements such as B, Mn, Se, and Al, which at toxic levels are responsible for reductions in the crop yields and consequently influence animal and human health. Fly ash application however might also decrease the uptake of heavy metals including Cd, Cu, Cr, Fe, Mn and Zn in plant tissues (Petruzzelli, 1986) which could be probably due to the increased pH of fly ash amended soil. Alkaline fly ash was also reported to act as binding agents for fixation of heavy metals and nutrients in waste and organic matters (Vincin *et al.*, 1994; Sharma *et al.*, 2007). In a like manner, Rautaray *et al.* (2003) observed lower concentration of Cd and Ni in both grain and straw of rice and attributed the reason to be the increase in soil pH due to application of fly ash to the rice crop which precipitated the native Cd, and Ni.

Boron toxicity is the major problem in agricultural use of ash (Page *et al.*, 1979). Lee *et al.* (2008) observed that in all fly ash treatment, B content in rice leaves and available B in soil at all growing stage were higher than those of control but all were below toxicity levels. Boron occluded amorphous iron and aluminum oxides were 20-39% of total B and were not influenced by fly ash application Most of the B accumulated by fly ash application was residual B which is a plant unavailable form and comprised >60% of the total B in soil. Patterson (2001) observed no significant concern over the uptake of boron, cadmium or zinc by barley or canola. Boron and zinc were within marginal to sufficient ranges for feed while Cd levels for barley and canola remained below the detection limit of 0.08mgkg^{-1} and 1.0 mgkg. Significant increase in K, S and Zn uptake were observed in analyzed plant samples. These same elements were also elevated within the soil sample. Maiti et al., (2005) have reported the relative abundance of bioavailable, acid extractable and total metals in fly ash in the order of Fe > Mn > Zn > Ni > Co >Cu. The variation of biological accumulation

coefficient of metals for plant (*Cynodon dactylon*) growing in the fly ash dyke was reported to be Fe>Zn> Mn >Pb>Ni >Cu > Co and Fe was the element most easily absorbed by plants.

The solubility of trace and heavy metals present in fly ash is <10% (Rohriman, 1971) however, 5-30% of toxic elements especially Cd, Cu, and Pd are leachable. The concentration of these elements in fly ash is very low; hence, the chance for leaching of these elements to ground water is negotiable.

Compared to common soils, majority of fly ash are not considerably enriched in radioactive elements or in associated radioactivity. Use of fly ash as soil ameliorant in place of lime could lead to reduction in CO_2 emissions, thus contributing to minimize global warming. Montes-Hermandez *et al.* (2008) demonstrated that 1 ton of fly ash could sequester up to 26kg of CO_2 . This confirmed the possibility to use this alkaline residue for CO_2 mitigation.

Swain and Padhi (2012) observed that N.P.K nutrient acquisition by guava increased with increasing level of coal ash but they did not vary significantly among the treatments. They attributed such additive effect of coal ash to efficient nitrogen, phosphorus and potassium assimilation in the presence of certain micronutrients in coal ash particularly copper and molybdenum and activities of certain enzymes (Marschner, 1996).

2.9.0. Soil Response to Boiler Ash Application

The effect of utilizing boiler ash as an agronomic amendment on soil properties have been studied by several workers (Inam, 2007). Results have shown that it may improve the physical, chemical and biological properties of soils and serve as a source of readily available plant micro and macronutrients Campbell, 1990; Aronsson and Ekelund 2004; Khan and Qasim, 2008). However, these changes in the properties of boiler ash amended soils vary with the characteristics of the ashes, different degrees of stabilization, different time scale, application rates, nutrient and metal loading within the soil profile and on the crop growth (Echler-Lobermann, 2010).

2.9.1. Effect of Boiler Ash on Soil Physical Properties.

2.9.1.1. Effect of boiler ash on soil texture

Application of high rates of fly ash can change the surface texture of soil usually by increasing the silt content (Jones and Amos, 1976; Basu *et al.*, 2009; Gray *et al.*, 2003). The hollow spheres of boiler ash replace bigger soil particles and make it possible for small silt sized particles to accumulate in voids, which modify the texture and pore structure.

The influence of boiler ash on physical properties of soil is primarily attributable to the changes in the texture of the soil (Ram *et al.*, 2007). Some researchers have observed that application of fly ash to sandy soil could permanently alter soil texture, increase microporosity and improve the water holding capacity (Page *et al.*, 1979; Ghodrati *et al.*, 1995). Addition of fly ash at 200t acre⁻¹ improved soil physical properties and shifted the USDA textural class of the refuge from sandy loam to silt loam (Buck *et al.*, 1990).

2.9.1.2. Effect of boiler ash on soil bulk density.

The particle size range of boiler ash is similar to silt and changes the bulk density of soil. Kalra *et al.* (1997) found that the dry bulk density of the soil decreased from 1.34gcm³ to 1.27gcm³ following the application of 40% ashes while textural class remains the same. The decrease in dry bulk density positively affected the water retention and moisture availability at the root zone. This ultimately results in better availability of plant nutrients and enhances plant roots proliferation in the soil.

Chang *et al.* (1977) observed that among five soil types, Reyes silt clay showed an increase in bulk density from 0.89 to 1.01CC⁻¹ and a marked decrease in soil having bulk density varying between 1.25 and 1.60gCC⁻¹ when the corresponding rates of fly ash amendment increased from 0% to 100%. Application of fly ash at 0%, 5%, 10% and 15% by weight in clay soil significantly reduced the bulk density and improved the soil structure, which in turn improves porosity, workability, root penetration and moisture-retention capacity of the soil (Kene *et al.*, 1991). Addition of fly ash up to 46% reduced the dry bulk density of soil in the order of 15-20% due to low specific gravity and unit weight of soil (Prabakar *et al.*, 2004).

In a study conducted by Kohli and Goyal (2010), fly ash was mixed with soil on w/w basis at concentrations of 0, 5, 10, 20, and 30% and used for growing of stem cutting of *Populous deltoids* for a period of four months. Mean bulk density of soil in the treatments receiving no fly ash application was 1.24Mg m⁻³ which decreased linearly with fly ash addition (R^2 = 0.99) to a level of 1.10Mgm⁻³ in the treatment receiving 30% fly ash. Kahra *et al.* (1997) reported that appropriately 69% of fly ash used in their experiment was made up of silt and clay fractions, silt loam in texture. The bulk density was 1.01Mg/m³ and a saturated hydraulic conductivity value of 3.57cm/d and water holding capacity of 56.9% (on weight basis). Also, Paterson (2001) reported that the bulk density of power plant wood ash supplied by Kraft pulp mill produced through incineration of wood wastes ranged from 0.35 to 0.88t/m³ with a mean of 0.48 ± 0.19, S.E 0.07.

2.9.1.3. Effect of boiler ash on pore size distribution and aggregate stability.

According to Letey (1977), the disposal of organic wastes in soil may affect the poresize distribution. This is because when large quantities of solid wastes are incorporated into the soil, they become a significant component of the matrix and can alter pore sizes. Erickson (1987) reported that the finer texture of ash increases total porosity and changed pore size distribution of sandy soil from macro- pores to a large percentage of meso-and micro- pores which retain more water under typical conditions.

Khan and Quasim (2008) reported that total porosity of a calcareous soil increased from 51.0 (control) to 52.10% at 250 tha⁻¹ fly ash rate .A gradual increase in concentration in a normal field soil (0, 10, 20 up to 100% V/V) was reported to increase porosity and water-holding capacity of soil (Khan and Khan, 1996). Amendment with fly ash up to 40% also increased soil porosity from 43% to 53% and water holding capacity from 39-55% (Singh et al, 1977). The finer texture of the ash increased total soil porosity and changed the pore size distribution of the predominately-sandy soil (Chirenje and Ma, 2002).

Haynes and Naidu (1998) reported that at low pH, acid soils are normally flocculated. As pH is raised by addition of wood-ash, the net negative charge on soil surface is increased and the ratio of negative to positive charges increases. At the same time AI^{3+} activity declines, as Al precipitates as hydroxyl ó Al polymers and as a result repulsive forces between particles dominant. The Ca in fly ash readily replaces Na at clay exchange sites and thereby enhances flocculation of soil clay particles, keeps the soil friable, enhances water penetration and allows roots to penetrate compact soil layers.

Undiluted bottom ash were however observed to induce dispersion of clays and other fine particles which are then dislodged and transported into pores, causing blockage and decreasing total porosity (Gros *et al.*, 2006). This was attributed to the increase for Na⁺ by up to 13% because of the bottom ash application. A decrease of the soil total porosity (-14%) was evidence of a subsequent adverse physical effect of this strong salinity.

Mba *et al.* (2010) observed significant differences in soil aggregate stability (AS) due to wood ash application. The highest AS value of 46% was observed in 6tha⁻¹ treatment in the first season. The value was 3.7 and 18% higher than 0, 2 and 4tha⁻¹ rates of application. In the second season, aggregate stability rate ranged between 36-44% with 6tha⁻¹ recording the highest values. Faleiros *et al.* (2014) reported that application of bagasse ash to soil at the

rates of 5, 10, 20 and 40Mgha⁻¹ (dry basis) caused no significant difference on soil aggregate stability index values.

2.9.1.4. Effect of boiler ash on soil hydraulic conductivity

Soil hydraulic conductivity plays a critical role in water management and in prediction of solute and contaminant transport in the environment. It has been confirmed experimentally that soil hydraulic conductivity depends among others, on its particle size distribution and specific surface areas as well as void ratio, swelling and ion exchange capacities (Egloffstein, 2001; Alamgir et al, 2005) and usually decrease with increase in content of fine particles (Alamigiri, 2005). Since boiler ash influence these properties, its addition to soils can be beneficial in reducing soil moisture transfer rates and increasing water retention. A study by Amiralian et al. (2012) revealed an effective role of fly ash in the reduction of hydraulic conductivity of sand. The hydraulic conductivity was reduced from 7.67×10^{-3} in pure sand to 9.65×10^{-4} at 10% fly ash application rate. Pathan *et al.* (2003) compared the hydraulic conductivities and water retention capacities of five fly ash samples and two coarse sands. Hydraulic conductivities of fly ashes were found to be between 105 to 248-fold lower than those in the soils. Water retention capacities at field levels were found to be three times higher in fly ash than those of soils. The work proved that benefits could be achieved at a 10% w/w fly ash amendment in soils (Pathan et al., 2003). However, it was noted that the considerable variability of fly ashes and soils supported the need for field trials before large-scale application of ash from a particular source.

Ayininuola and Olasebikan (2013) reported that rice husk ash (RHA) decreased coefficient of permeability of soil due to action of exchangeable cations such as Al^{3+} and Ca^{2+} present in the ash with monovalent ions forming strong bond that hindered passage of water.

2.9.1.5. Effect of boiler ash on rheological properties of soil.

Rifa et al (2009) observed that increasing coal ash in a coal ash-soil mixture causes the decreasing of liquid limit and plasticity index and swelling potentials. In a study on stabilization of tropical lateritic soils using self-cementing coal fly ash (Okunade, 2010) observed for all the soils that increasing coal fly ash contents brought about increasing improvement in the plasticity and mechanical properties of the soils. When comparing the average value at 12.5% coal ash content, there was a reduction in the liquid limits from 39.0% to 33.3%, a reduction in the plasticity indices from 15.3% to 9.3% Mba *et al.* (2013) reported that application of wood ash, rice, husk ash and coconut ash at 4tha⁻¹ significantly (P=0.05) increased soil liquid limit (LL) and plastic limit. Observed liquid limit values were 6%, 12% and 11% higher in coconut ash, rice husk ash and wood ash amended plots respectively relative to control.

2.9.1.6. Effect of boiler ash on soil water retention

Soil water retention is a major soil hydraulic property that governs soil functioning in an ecosystem and greatly affects soils management. Modification of soils by management such as application of ash can change soil organic matter content and composition, which may affect both soil structure and absorption properties of the soil.

Etiegni *et al.* (1991) studied wood ash structure and its changes during wetting. They suggested that ash is essentially hydrophilic with particle swelling through hydration of oxides to form new compounds. After four weeks of wetting, expansion had increased the volume by 12.5% on the original. The effect they noted could be both beneficial and detrimental in soils where ash might be used as soil amendment. In clay soils, small pores might easily be clogged by wetted ash causing decreased aeration but in sandy, free draining soils, this water holding capacity could be very beneficial to plant growth.

Percentage moisture retained at saturation, field capacity and wilting point expressed on weight basis increased with fly ash addition (Kalra *et al.*, 2007). Chirenje and Ma (2002) reported that boiler ash increased the soils water holding capacity significantly at 0-1500cm suction. For the control soil, the moisture content at field capacity and permanent wilting point (100 to 300cm suction) were 8 and 14% respectively (6% plant available water). The corresponding value for the ash amended soils were 10 to 16% (6% plant available water) and 30 to 42% (12% available water) in 900 and 1800Mgha⁻¹ treatments respectively. Under typical dry soil conditions above 300cm suction, the ash amended soil contained 10 to 30% moisture compared to <8% for the control. Application of high rates of ash therefore increases the chances of plant survival under conditions of extended water stress in soil.

Fly ash has also been shown to increase the plant available water in sandy soils (Taylor and Schumann, 1988). Singh and Siddiqui (2003) reported that mean water holding capacity (W/W) of soil in treatments receiving no fly ash application was 39.8% which increased linearly (R^2 =0.97) with fly ash application rate. Amendment with fly ash up to 40% increased water-holding capacity from 39 to 55%. Fly ash has also been reported to increase the water holding capacity of sandy loamy soils by 8%, which in turn caused improvement in hydraulic conductivity and thereby help in reducing surface encrustation. Ghodrati *et al.*

(1995) attributed the improvement in water holding capacity of fly ash amended sandy soil to the silt-sized particles of the fly ash. In addition, Jamil and Quasim (2008) reported that the decrease in dry bulk density and improvement in soil porosity positively affect the water retention and moisture availability in the root zone. This ultimately results in better availability of plant nutrients and enhances plant root proliferation in the root zone.

Grewal *et al.* (2001) found that fly ash application results in greater moisture storage in the plough layer of soil at all stages of corn growth. A study by Sarkar and Rano (2007) revealed that fly ash obtained from a thermal power plant working on stoker fired combustion produced the highest water-holding capacity followed by the one working on pulverized fuel combustor. Fly ash collected from super thermal power plant had the least water holding capacity (40.7%). The coarser size fractions of fly ashes in general comprised higher water holding capacity than the finer one.

2.9.1.7. Effect of boiler ash on soil electrical conductivity.

Soil electrical conductivity depends on the concentration of Na⁺, Cl⁻, HCO₃⁻, So₄⁻² and HBO₃⁻ and their ability to conduct electricity (Wolf, 1990). Addition of graded doses of fly ash has been reported to increase the electrical conductivity values of soil (Kishor *et al.*, 2010; Carlile *et al.*, 2013; Das *et al.*, 2013. Increasing electrical conductivity values of soils due to fly ash addition may be attributed to the fact that the soluble salts from fly ash might have dissolved in soil moisture and thereby increased the ionic concentration of the soil solution (Selvakumari *et al.*, 2000).

In a study by Chirenji and Ma (2002), the electrical conductivity in the surface soil increased by up to two orders of magnitude in all fly ash treatments (8.6 to 9dsm-1) compared to the control of 0.02dsm-1) indicating that significant accumulation of soluble salts in the soils. However, up to 50 times reduction in electrical conductivity in the surface soil was observed after only four months of leaching. Sodium and potassium salts are very soluble and thus leached out quickly resulting in significant reduction in electrical conductivity (K decreased from 700 to <200mgkg⁻¹ in the 1800mgha⁻¹ treatment(s). They also observed that the electrical conductivity values of the lower parts of the profile were up to three times higher than that of the surface at the end of the study, indicating that the salts were still migrating through the soil. Patterson (2001) on the other hand reported that ash with electrical conductivity (50.3 dsm-1) significantly increased electrical conductivity at all

ash treatments in the first two years after ash application but levels decreased to levels similar to that before the application of wood ash

According to CFRI (2003) change in soil electrical conductivity resulting from amending soil with fly ash in India ranged from 0.42-4.29 (dsm-¹). Kalra et *al*.(1997) in a study, reported that addition of fly ash to the soil increased electrical conductivity from 0.467 to 0.746 (mmhos/cm) while, Jamil and Quasim (2008) reported that electrical conductivity increased from 0.38dsm⁻¹ to 1.50 dscm⁻¹ in the treatment receiving 250tha⁻¹ boiler ash. Similarly, Vest *et al.* (1999) reported that electrical conductivity was about 6 times higher than the control when treated with 896 and 1792 Mtha⁻¹ of boiler ash.

Saline soil induces physiological and metabolic disturbance in plants affecting development, growth, yield and quality of plants (Jouyban, 2012). As such soil with electrical conductivity $>2dsm^{-1}$ is considered to be saline and would be unsuitable for ash application (Alberta Environmental, 1994). Boh *et al.* (2013) observed that salinity stress significantly decreased maize plant height and shoot dry weight but application of wood ash at 150Mgkg⁻¹ soil proved suitable to foster sodium and salt tolerance of maize when salinity does not exceed 4.2dsm⁻¹.

2.9.1.8. Effect of boiler ash on soil erosion

Boiler ash when applied in large quantity increases soil erodibility. Gorman *et al.*, (2000) found that fly ash amended spoil had much greater erosivity than un-amended spoil. The high erosivity was attributed to silt grain size, spherical particles and lack of initial aggregation. Silt-sized soil particles are highly erosive and erosivity with boiler ash is even greater due to the largely spherical shape of the ash particles. These authors caution that while large fly ash applications may improve pH and water holding capacity, special precautions to reduce soil erosion potential are required (reduced slope gradient, length, and combining ash with organic amendments). Reichert and Norton (1994) however, observed that the application of fluidized bed combustion bottom ash reduced total water loss by 1.1 to 2.0-folds and total soil loss by 1.5 to 3.9-folds.

Surface ash particles cause a structural soil seal to form (Etiegni and Campbell, 1991). Mallik *et al.* (1984) reported that soil sealing by ash particles increase run off and sediments through pore clogging by the physical movement of fine ash particles. The hydraulic conductivity of the seal or crust can be several orders of magnitude lower than that of underlying soil (Assouline, 2004).

2.9.2. Effect of Boiler Ash on Soil Chemical Properties.

2.9.2.1. Effect of boiler ash on soil pH

The presence of alkali metals, alkaline earth metals, chlorine, sulphur and silicon in ash influences its reactivity and leaching to the inorganic phases (James *et al.*, 2012). Boiler ash has been shown to act a liming material to neutralize soil acidity and provide plant-available nutrients (Taylor and Schumann, 1988). Application of large quantities of wood boiler ash to soil increases soil pH and salinity, and may affect plant w/ater and nutrient relations (Phung *et al.*, 1978; Vest *et al.*, 1999). Raison (1979) attributed the ability to neutralize acidity in soils by ash to accretion as ash residues are generally dominated by carbonates of alkali and alkaline earth metals, variable amounts of silica, heavy metals, sesquioxides, phosphates and small amount of organic and inorganic N. Another reason could be because of high surface area and porous nature of boiler ash that increases the CEC of the soils. Thus, there could be a chance for Al and Fe to bind with the exchange site of the soil. Nottidge et al. (2006) also reported a linear increase in soil pH with the amount of ash added to the soil because of substantial reduction in soil exchangeable aluminium.

The liming potential (i.e. ability to increase soil pH) by wood ash application) differs due to differences in the soils buffering capacity (Brady and Weil, 1999). Studies evaluating the effect of wood ash application on soil pH have found minimal differences (i.e. up to 0.5 units) between ash application rates of 10 to 30tha⁻¹ (Naylor and Schmidt, 1989; Muse and Mitchell, 1995). However, higher pH leads to solubilization of organic matter and has a negative impact on soil biota. Dissolved organic C forms complexes with metals from ash (Sauve *et al.*, 1997) and increases their mobility especially under conditions of high ionic strength.

Buddhe *et al.*(2014) did not observe a significant increase in soil pH amended with fly ash based soil conditioner (Biosil). They noted that the low response of soil may be due to very low rate of application of Biosil and that was at the first year of application. Kumar (2002) studied the possibility of fly ash application to agricultural soils. The result revealed that fly ash application particularly in higher amounts (8% w/w) increases the pH and electrical conductivity of the soils, however the application of low amount (2% and 4% w/w) favored plant growth and improved yield. In a two-year study, relative to the control, sole application of wood ash increased pH linearly with rates of wood ash (Agbede and Adekiya, 2012). Khan and Qasim (2008) reported a slight increase in soil pH in control (8.2 to 8.90) in the treatment receiving boiler ash at 250tha⁻¹ rate. [\

Applications of bottom wood ash (BWA) significantly increase the pH of soils. In a sandy soil the pH increases was 0.43 units after two seasons with application of BWA, while pH increases by 0.23 in the sandy loam soil which had higher buffer capacity. However, in a ryegrass experiment on sandy loam, the BWA application leveled out a pH decrease caused by N application. Similar pattern was observed in the experiment on sandy soil. (Haraldsen et *al*.2012).

Kalra *et al.* (1997) observed a pH decrease from 8.31 for the control (no ash) to 7.98 for 40% ash whereas the respective electrical conductivity (mm hos/cm) and organic carbon (%) values increased from 0.46 to 0.746 and 0.28 to 0.31%. The pH of surface soil also decreased from 9.5 and stabilized at approximately 8.6 after the initial seven months due to leaching of easily leachable K and Na carbonates that buffer pH was at very high values (Chirenje and Ma, 2002). They observed very little change in pH in the subsequent 14 months showing that the CaCO₃ was still present in the soil in large quantities> (10%) since soil clay and organic matter generally protect carbonate from dissolution. In addition, they claimed that most micro nutrients precipitate out of solution at this high pH of 8.6. Boiler ash should therefore be applied based on liming equivalence to avoid this problem.

In general, pH increase with time and higher concentration of wooden ash up to 48 tha⁻¹ of stabilized ash (Krakow, 2010). Addition of wood ash to soil increased pH by 0.3 - 1.4 during the first week and 0.1-1.0 the second week with addition of stabilized ash compared to control. Corresponding numbers were 0.3 - 3 and 0.4 - 0.9 respectively. The author noted that pH increase more rapidly with addition of fresh ash compared to stabilized ash during the first two weeks of testing.

In a similar manner, Chirenje and Ma, (1999) observed that soil pH increased from 5.6 in the control pots to above 9.4 in the ash amended pots after six weeks but this went down to around 8.5 after eight months. The pH did not go below 8.5 even after 20 months of natural leaching in the field due to the persistence of mainly un-dissolved $CaCo_3$ into the soil. Saarsalmi *et al.* (2001) reported an ash induced pH increase of 0.6-1.0 pH unit in a humus layer 16years after wood ash application. In the mineral soil, the increase was observed later than in the humus.

Adjei-Nsiah (2012) also reported an increase of soil pH from 4.8 (control) to an average of 5.8-5.9 at 110 days after the application of palm bunch ash (PBA). The increase in the pH was attributed to the pH level of the PBA and also due to decrease in Al $^{3+}$ as a result of precipitation of Al as hydroxyl Al (Mbah *et al.*, 2010).

Application of combined cocoa pod husk ash; poultry droppings and N.P.K 20:10:10 fertilizer increased soil pH relative to control at 30, 60, 90 days of incubation. The pH was highest irrespective of days of incubation when higher level of cocoa pod ash (10tha⁻¹) was included in the treatment formulation. The highest pH was given at $C_5P_{10}F_{100}$ at 30days and $C_{10}P_{10}F_{100}$ at 60 and 90 days of incubation.

2.9.2.2. Effect on soil nutrient status.

Several researchers have reported that total and plant available macro-nutrients (Ca, Mg, K and P) and micronutrients (Fe, Mn, Cu, and Zn) increased substantially in soil after ash application under both field and greenhouse conditions (Naylor and Schmidth, 1989; Vest *et al.*, 1999; Rautaray *et al.*, 2003; Adeji-Nsiah and Obeng, 2013; Buddhe, 2014). However, their downward movement through soil column and their availability for plant growth became limited to a depth of 80cm from the soil surface (Menon *et al.*, 1992).

Kahl *et al.* (1996) studied the nutrient change over time in the soil solution chemistry sampled by lysimeters beneath white birch and American beech woodland. The soil solution shows minimal effects at low ash dose rate, but heavier additions overload the soils buffer capacity. Swift increases in Ca, Mg, Cl, N0₃ and S0₄ were sustained to the end of the experiment in case of the maximum load. There was, however, no effect of leaching of trace metals. This may have accounted for why Paterson (2001) observed minimal differences in soil available nutrient levels between12.5 and 25tha⁻¹ ash application rate. Similarly, Krakow (2010) reported that ash leachate showed significant elevated concentration of Cu, Mn and SO₄ compared to the control.

Soil organic carbon (SOC) is the most often reported attribute and is chosen as the most important indicator of soil quality and agricultural sustainability. Das *et al.* (2013) reported that organic C increased significantly with every subsequent increase in doses of fly ash over the control. The soil organic C tended to increase significantly when fly ash was applied alone in comparison to fly ash integrated with recommended dose of fertilizer and FYM. This was attributed to faster oxidation (decomposition) of fly ash under the influence of chemical fertilizer and FYM (Brady, 1995).

Buddhe *et al.* (2014) also reported that refined magnetized fly ash \Rightarrow Biosilø improved organic-C of soil by 0.65% in T₁₅₀ to 7.8% in T₄₋₆₀₀ over the initial value (0.64% organic carbon) as well as over recommended dose of fertilizer control (0.64% organic carbon). The initial potassium content of 297kgha⁻¹ observed to increase to 303kgha⁻¹ in T₆₋₉₀₀ treatment showing 2.02% increase while the content of phosphorus markedly increased over initial

status of 17.45kgha-1 due to increasing doses of Biosil but there was non-significant influence on nitrogen content.

Application of graded levels of coal fly ash with or without recommended dose of NPK fertilizer increased the soil content of organic C, N, K, Ca, Mg, P, Zn, Fe, Mn, and Cu (Yeledhelli *et al.*, 2007). Addition of saw dust ash to urea increased the availability of OM, N, P, K and Ca in soil (Abdulraheem *et al.*, 2012). While, cocoa pod husk ash was found to increase soil OC, N, NH4^{-N}, NO3^{-N}, available P and exchangeable K, Ca and Mg (Adejobi *et al.*, 2011). When combined with 200kgha⁻¹ NPK, soil nutrient such as % OC, % total N, and exchangeable K were also increased (Akinmutimi, 2014). But combining it with poultry droppings and NPK 20: 10: 10 fertilizer, significantly increased(P< 0.05) soil organic C, N, N03^{-N}, N03^{-N}, NH4^{-N}, available P at 30, 60 and 90 days of incubation (Ayeni and Adeleye, 2009). Oil palm bunch ash and their combined use with NPK fertilizer at reduced level have been reported to increase soil Om, N, P, K, Ca, and Mg (Ojeniyi, 2010). The single effect of wood ash and their combination with poultry droppings, cow dung and NPK (20: 10: 10) significantly increased soil pH, available phosphorous, exchangeable acidity and % base saturation of the amended soil (Nwachukwu *et al.*, 2012).

Fly ash and acidic soils have high p-fixation capacities (Ram *et al.*, 2011) This is in agreement with Paterson (2001) who claimed that very little of applied P in ash is in available form and as such has little or no effect on available P. This effect was attributed to the rate at which P contained within the ash is made available for plant uptake and suggests that available P is gradually released overtime with the plants taking up P as it becomes available.

Das *et al.* (2013) reported that available P content of the soil increased with increase in the quantity of fly ash added to the soil due to the high content of available P in the fly ash. The favorable effect of fly ash on P availability was ascribed to its effect on biotic activity. Jala (2005) reported good adaptability of phosphate solubilizing bacteria in fly ash amended soils and better survival exhibiting 36.4% to 86.1% phosphorous solubilization. It has also been observed that Si present in fly ash play a significant role in releasing P to available pool from the insoluble sources in fly ash as well as soil (Matte and Kene, 1995).

Scheimenz *et al.*, (2011) reported that the supply of ash in soil increased soil P pools (total P, water-soluble P and P saturation. However, Ohno and Erich (1990) claimed that the amount of P released during the incubation of wood ash within the soil profile was related to soil pH but reactions of P determine its availability.

Adeji-Nsiah and Obeng (2013) reported increased availability of P content of the soil with increased application of palm bunch ash. This was attributed to release of P from complexes of Al and Fe under increasing soil pH (Mbah *et al.* 2010, Adeji-Nsiah, 2012).

Macronutrients like Ca, K, and Mg exhibit different solubility in ash amended soils (Ghodratic *et al.*, 1995). According to Khan and Khan (1996), addition of fly ash in the normal field soil increased pH, thereby improving the availability of sulphate, carbonate, bicarbonate, chloride, P, K, Ca, Mg, Mn, Cu. Zn, and B. They also found that addition of fly ash to acidic and alkaline soil decreased the amounts of Fe, Mn, Ni, Co, and Pd released from acid soil. However, the release of these metals from alkaline soil remained unchanged. Haraldsen et al. (2012) reported that application of bottom wood ash significantly increased the level of residual readily available P, K, Mg in both pot and field experiments.

Rani and Kalpana (2010) reported buildup of micronutrients cations in soil due to application of fly ash. Metals like Fe, Zn, Cu, Mn, Ni and Cd have been shown to be available at higher concentrations in DTPA extracts of fly ash (Gupta *et al.*, 2007). It has been observed that surface application of wood ash was able to reduce Ca (N0₃)2 extractable Zn in the subsoil from about 50Mgkg⁻¹ in the control to less than 4mgkg⁻¹. The reduction of concentration of Zn in the soil solution indicates a reduction in phytotoxicity (Brown et al., 2003).

Jamil *et al.* (2004) attributed the increase in the number of productive tillers of wheat to the alleviation of deficiency of some of the essential nutrients after the addition of baggase ash to soil. Similarly, the increase in the growth traits of Guava (Psidium guajava L.) in coal ash amended soil has been attributed to nutrient acquisition by the plant (Swain and Padhi, 2012).

2.2.10. Effect of boiler ash on soil biological properties.

The study of the effects of ash on soil biological properties is not as extensive as on soil physico-chemical characteristics. Ash modifies the biological activity of soil indirectly through its influence on pH, electrical conductivity, salinization, boron and toxicity of other toxic elements, and its influence on soil physical condition especially textural improvement (Ram *et al.*, 2011, Tsadilas, 2014).

Yeledhelli *et al.* (2007) reported that coal fly ash modified the soil bacterial count, and its effects depends on the level of fly ash applied, the microbes under study ,and the total microbial population (bacteria fungi and actinomycetes). They noted that application of fly

ash did not affect the microbial population adversely. Even though there was an increase in soil pH, its effects was negated by improvements in physical conditions and due to supply of some essential trace elements for growth of microorganisms

Zimmermann and Frey (2002) found an increase in microbial activity and biomass in soil treated with wood ash as well as an increase in the growth rate of soil microorganism. The authors concluded that increased pH and quantity of nutrients following wood ash application were closely related to the result in the investigation. The higher activity was also linked to increased mineralization of organic matter.

Mahmood *et al.* (2003) observed that bacterial activity and community structure measured as changes in phospholipids fatty acids (PLFA) composition were significantly greater in ash treated soils. Garampalli et al. (2005) carried out a study on the effect of fly ash at three concentrations viz: 10, 20 and 30g FAkg⁻¹ soil on the infectivity and effectiveness of vesicular arbuscular mycorrhizzal (VAM) and Glomus aggregation in pigeon pea (Cajanus cajan L.) maruti. All the concentrations of fly ash amendment in soil were found to significantly affect the intensity of VAM colonization inside the plant roots. At higher concentrations (30g FA kg⁻¹ soil), the formation of VAM fungal structure was suppressed completely.

Pati and Sahu (2004) studied the effect of seven concentrations (0, 2.5,10, 15, 25 and 50% w/w) of fly ash on the toxicity test of earthworms (Drawida wittsi). Using CO_2 evolution and enzyme activities (dehydrogenase protease and amylase) in the presence or absence of D. Wallsi, they found little or no inhibition of soil respiration and enzyme activities up to 2.5% FA amendments. With further addition of FA, all the above were significantly decreased. On the other hand, significant stimulation of soil respiration and microbial activities were observed up to 5% FA when soil contained earth worm. This may be due to increased microbial activities (Urease and Cellulase).

Kohli and Goyal (2010) also observed that application of fly ash as an amendment at 10% was found to be optimum for bacterial population, soil dehydrogenase activity and microbial biomass. Similarly, Sarangi *et al.* (2001) reported that invertase, amylase, dehydrogenase and protease activity increased with increasing application of fly ash up to 15tha y^{-1} but decreased with higher levels of fly ash application.

On the contrary, Schutter and Fuhrmann (2001) reported that dehydrogenase activity decreased at all concentrations of fly ash as compared to control in the beginning and only at 10% fly ash, it tends to show increase after 22 weeks of incubation. These detrimental effects were partly due to excessive levels of soluble salts and trace elements present in un-

weathered fly ash. However, high concentrations of salts and other elements may decrease as the fly ash becomes weathered during natural leaching processes thus reducing detrimental effects overtime (Adriano *et al.*, 1980, Sims *et al.*, 1995).

Addition of un- weathered fly ash to sandy soil severally inhibited microbial respiration, number, size, enzyme activity and soil nitrogen cycling such as nitrification and N nitrogen mineralization (Wong and Wong, 1989; Garau *et al.*, 1991). These adverse effects were attributed to the presence of excessive levels of soluble salts and trace elements in unweathered fly ash. However, the detrimental effect was reduced over time as the concentration of the soluble salt was reduced by natural leaching (Sims *et al.*, 1995). The use of extremely alkaline ash (pH 11-12) was also suggested as one of the reasons for those adverse effects.

The application of lignite fly ash also reduced the growth of seven soil borne pathogenic microorganisms whereas the population of Rhizobium Sp and P-solubilizing bacteria were increased under the soil amended with either farmyard manure or fly ash individually or in combination (Schutter and Fuhrmann, 2001).

CHAPTER THREE

MATERIALS AND METHODS

3.1.Site Description

3.1.1. Location

The study was conducted at the Research Farm of the Department of Soil Science, Faculty of Agriculture, University of Nigeria, Nsukka. The site is located by Latitude $06^0 25$ N and Longitude $07^0 24$ E and at an altitude of approximately 400m above sea level.

3.1.2. Climate

Generally, the area of the study is within the humid tropical climate characterized by mean annual rainfall of 1550 mm. The rainfall distribution is bimodal and falls between April and October while the dry season is between November and March. It is characterized with mean annual maximum (day) and minimum (night) temperatures of 31^oC and 21^oC respectively, while the average relative humidity is rarely below 60 %.(Ezeaku and Egbemba, 2014). The mean annual evapo-transpiration (ET) is about 1560mm and exceeds total rainfall in most months of the year (Igwe, 2004). The mean solar radiation varies from 209 to 325 cal/cm² day and sunshine duration from 3.3 to 7.6 hours.

3.1.3. Agriculture and Vegetation

Grassland vegetation is predominant in the study location, which according to Mbagwu (1991) is within the forest savanna transition vegetation zone. It can be described as derived savanna. The various types of arable crop widely grown in the study area include maize (*Zea mays*), yam (*Dioscorea spp*), cassava (*Manihot esculentum*), cocoyam (*Colocasia esculentum*), pumpkin (*Cucurbita pepo*), lima bean (*Phaseolus spp*), melon (*Cucumeropsis edulis*), pumpkin (*Telferia occidentalis*) and garden egg (*Solanum macrocarpum*). Others are okro (*Hibiscus esculentus*), African spinach (*Amaranthus hybridus*), pepper (*Capsicum annum*), sweet potato (*Ipomea batatas*), bitter leaf (*Veronia amygdaline*) and tomato (*Lycopersicon esculentum*) (Ugwu, 2006).

3.1.4. Geology

Geologically, the site has been classified as the upper coal measures (Nsukka formation) Nadian and False-bedded Sandstone (Ajalli sandstone) Macstrichtian (Orajiaka, 1975).

3.1.5. Soil

Morphologically, the soil is very deep, dark, reddish brown in the epipedon and red in the sub soil. They are coarse to medium textured, granular in structure, acid in reaction and low in nutrient status. The soil temperature regime is isothermic (i.e. $> 22^{\circ}$ C) and the moisture regime is Ustic. It is an Ultisol belonging to the Nkpologu series and classified as Typic kandiustult (Akamigbo and Igwe, 1990). It requires liming, addition of organic and inorganic fertilizers for profitable rain fed agriculture.

3.2. Materials Used

Boiler ash used as soil amendment was collected from Solive Vegetable Oil Mills Ltd, Nsukka. It was generated from burning oil palm mill wastes (palm kernel shells, cakes, sludge etc.) in boilers for biomass energy generation. The poultry dropping was collected from Newera Farms Nsukka. A hybrid maize (*Zea mays* L.) variety (Oba supper II) obtained from Premier Seeds Ltd was used as a test crop. It was chosen based on its sensitivity to a wide range of contaminants (Wong *et al.*, 1991), short maturation, sensitivity to soil nutrient status and common use in the study area.

3.3. Soil Sampling and Storage

Soil samples were collected from the experimental site (0.058 ha) at three phases. The first sampling was done before the trial establishment at 0 - 20 cm soil depth for the determination of the physico-chemical properties. Second and third soil sampling was carried out at the end of the first and second cropping seasons. The samples were collected at the centre of each plot according to the treatments. These were air-dried, passed through a set of 4.75 and 2mm sieves. The 4.75 -2.0 mm aggregates were used for determination of soil aggregate size distribution and stability, while the < 2mm fine earth fractions were collected and stored for use in the determination of particle size distribution and chemical properties.

Soil cores were also collected in an undisturbed state at three phases. Three soil core samples were randomly collected from the experimental site before treatment application. At the end of the first and second cropping seasons, one core sample was collected from the centre of each plot. These samples were collected with metal core rings (117.86 cm³) by hammering the sharp end carefully into a flat surface within the plots. The cores were dug out with a trowel and the soil was trimmed with a knife and covered one end with a piece of cloth. These samples were used for the determination of bulk density, porosity, soil moisture characteristics, and saturated hydraulic conductivity.

3.4. Boiler Ash Sampling

Sampling of the ashes was carried out over a period of three days and the individual samples (1kg per sampling day) were combined to give one composite sample weighted 3kg. The sampling period represented a normal process operating conditions for the combustion plant e.g. in terms of oxygen content and temperature. A cone and quartering method (Gerlach *et al.*, 2002) was repeatedly applied to obtain a homogenous mixture.

3.5. Determination of Physical Properties of Boiler Ash, Poultry droppings and Soil Samples.

3.5.1. Determination of particles size analysis of boiler ash

The particle size distribution of the BA was determined using the (American Society for Testing and Materials (ASTM) Designation C. 1136 specifications. 100g of the dried ash was taken and introduced unto a set of sieves (4.00mm, 2.0mm, 1.00mm and 0.5mm mesh) arranged in descending order of fineness and shaken for 15 minutes which is the recommended shaking time to achieve complete classification. The weight retained on each sieve was taken and the value expressed as a percentage of the weight of the initial sample.sieved.

3.5.2. Determination of particle size distribution of soil

Analysis of particle size distribution of the < 2mm fractions was done by the Bouyoucos hydrometer method as described by Gee and Bauder (1986) using sodium hexametaphosphate.

3.5.3. Determination of bulk density of soil

After oven drying the soil sample used for the saturated hydraulic conductivity measurements to constant weight at 105°C, soil bulk density was determined by the core method (Blake and Hartage, 1986) using the formula,

BD $(g \text{ cm}^{-1}) = M_S / V$

Where, $BD = bulk density (gcm^{-3})$

MS= mass of dry soil sample (g)

V =Volume of sample (cm^{-3})

The soil volume is equivalent to the volume of the core.

 $V = r^2 h$

Where V = volume of core = volume of soil.

= constant 3.142

r = radius of the core

h = height of the core

3.5.4. Determination of bulk density of boiler ash and poultry droppings

The method of self-compacting (Brazil, 2007) was used to determine bulk density of BA and PM. A 500 ml plastic beaker was filled to the 300 ml mark with substrate. Then, this cylinder was lifted and dropped 10 times, falling under the action of its own weight from a height of 10 cm. With a spatula, the surface was slightly leveled and the volume (ml) read. Then, the material was weighed (g) by subtracting the mass of the beaker. The moisture of each material used in the self-compression was determined, to calculate the density based on dry weight. The procedure was repeated three times using different subsamples.

3. 5.5. Determination of saturation moisture percentage of soil, boiler ash and poultry droppings

This was calculated using the formula,

Saturation moisture percentage = (mass at saturation - oven dry mass) / mass of soil or boiler ash or poultry droppings only x 100.

3. 5.6. Determination of saturated hydraulic conductivity and permeability of soil

A set of undisturbed core samples were collected with metal core cylinders, (117.86 cm³) for the determination of hydraulic conductivity. Soil saturated hydraulic conductivity (Ksat) was determined on the intact core samples and Ksat computed from the equation (Reynolds, 1993);

Ksat = $QL/At.\hat{e}H$

Where:

Ksat =Saturated hydraulic conductivity, cm/l

Q = volume of water, cm³

A = cross sectional area of sample (cm)

L = length of soil column, cm

h = Height of water above soil column

 \hat{e} H = hydraulic head difference (l+h), cm

t = time, min

In this method, a flask of water was inverted above a core, containing water in order to maintain constant head of water. The quantity of water (Q) drained in every 5 minutes was measured until equilibrium (constant flow of water) is reached.

The values of Ksat were used to compute the values of permeability as follows:

$$Kp = Ksat. X (/ g)$$

 $Kp = permeability cm^2$

Ksat = see equation above

= viscosity at $27^{\circ c^{-}}(0.00855 \text{ g cm}^{-1} \text{ sec}^{-1})$

 $\rho = \text{density of water, gcm}^{-3}$

 $g = acceleration due to gravity (980 cm sec^{-2})$

3.5.7. Determination of total and air porosity of soil

Soil total porosity was calculated from the relationship between bulk density and particle density. Particle density (ρ p) was assumed 2.65 g cm⁻³ for most mineral soils (Foth,1990).

 $ST = (1 \circ \rho b / \rho p) \times 100$

ST = Total porosity (%)

 $\rho b = \text{bulk density} (\text{Mg cm}^{-3})$

 $\rho p = particle density(Mg cm^{-3})$

Air porosity is the space occupied by air when the sample is at field capacity (that is at 0.1 bar suction for sandy soils). It is expressed as percentage of the sample volume and calculated thus:

 $S = St \circ Qv (0.1)$

S = air porosity (or macro porosity) (%)

t = Total porosity(%)

Q V. (60cm) = percentage volume of water held at 60cm suction (that is field capacity, %)

3.5.8. Separation of water- stable aggregates of soil

The method of Kemper and Rosenau (1986) was used to separate the water-stable aggregate (WSA). In this method, 20g of the < 4.75mm air-dried aggregates were placed on top of a net of four sieves of 2, 1, 0.5, and 0.25mm mesh size and soaked in distilled water for 10 minutes. The sieves and their contents were then oscillated vertically for 20 times along a 4cm stroke at the rate of 10 scillation per second. After wet sieving, the aggregates retained on

the sieves were oven-dried at 105° c. The mass of the < 0.25mm fraction was obtained by difference. Later, they were mixed together, placed in a (0.25mm) sieve, and washed with water to obtain the weight of sand fraction.

The respective dry masses were used to compute mean weight diameter, percentage water-stable aggregates, and state of aggregation.

Mean Weight Diameter (MWD

 $MWD = \hat{U} WiXi$

Where xi = arithmetic mean diameter of the i-1

I= sieve openings (mm)

W (i) = proportion of the total sample weight (Uncorrected for sand and gravel,

occurring in the fraction) (dimensionless).

n= total number of sieve fractions (in this case 5).

Larger MWD value indicates higher proportion of macro-aggregates and therefore, higher stability to water erosion. The mean weight diameter (MWD) is also an index that characterizes the structure of a whole soil by integrating the aggregate size class distribution into one number. The MWD indicates the effect of different management practices on soil structure (Six et al., 2000).

State of aggregation = (WSA ó mass of sand)/ Mass of sample x 100

Water stable Aggregates (WSA)

% WSA = (Retained soil aggregate ó sand weight/ (Soil sample=Total sand) x 100

3.6. Determination of Chemical Properties of Boiler Ash, Poultry droppings, Soil and Maize Grain Samples.

3.6.1 Determination of organic carbon and organic matter

The organic carbon was determined by the Walkley ó Black procedure as described by Nelson and Sommers (1982) and this was converted to soil organic matter by multiplying the percentage organic carbon by 1.724

3.6.2. Determination of total nitrogen

Total nitrogen was determined by the macro Kjeldahl method as described by Bremner (1996) using $CuSO_4/Na_2SO_4$ catalyst mixture. The ammonia from digestion was distilled with 45% NaOH into 2.5% boric acid and determined by titrating with 0.05N HCl.

3.6.3. Determination of pH

10g each of the samples was weighed in duplicates one for analysis with water and the other with 0.1N KCl. 25ml of deionized water and added to the weighed soil samples and to the duplicate 25ml of 0.1 KCl was added. The value was read using Beckman Zeromatic pH meter (Peech, 1965).

3.6.4. Determination of available phosphorus

Available phosphorus was determined by Bray II method as described by Bray and Kurtz (1945).

3.6.5. Determination of soil exchangeable bases and cation exchange capacity (CEC)

Exchangeable bases (Na⁺, K⁺, Ca²⁺ and Mg²⁺) were extracted with 1N ammonium acetate solution .Ca and Mg were determined by atomic adsorption spectrometer while K and Na were determined using flame photometer. Cation exchange capacity (CEC) was determined by washing the NH_4^+ saturated soil sample free from NH_4OAC with methanol and distilling the exchangeable NH_4 with water and MgO in to boric acid solution (Rhodes,1982).

3.6.6. Determination of soil exchangeable acidity $(AI^{3+} + H^{+})$

Exchangeable acidity $(AL^{3+} + H^{+})$ was determined by the titrimetric method of Mclean (1965).

3.6.7. Determination of base saturation.

It was obtained by dividing total exchangeable bases by cation exchange capacity and multiplying by100.

3.6.8. Determination of electrical conductivity (EC)

Electrical conductivity (EC) was determined by the method described by Rhoades (1996). 10g each of the samples was weighed for analyses. 25ml of deionized water was added to the weighed soil sample and stirred. The EC values were obtained using an electrical conductivity meter.

3.6.9 Determination of exchangeable sodium percentage (ESP) and sodium absorption ratio (SAR)

Exchangeable sodium percentage (ESP) and Sodium absorption ratio were calculated using the following equations.

ESP = (Exchangeable Na+/CEC) X100

SAR=Na⁺/ç (Ca²⁺+Mg²⁺)/2

3.7. Land Preparation

The experiments were conducted in two successive cropping seasons of 2013 and 2014. The area has been under fallow for more than five years. It was demarcated into blocks and plots with fortified bounds to minimize soil erosion and nutrient mobility to adjacent plots. Each plot had a dimension of 4m length by 3m width, giving an area of 12m². In the second year, the plots were prepared by hand hoes so as not to disturb the plot boundaries.

3.8. Experimental Design and Treatments

The experiment consisted of sixteen treatments laid out in a Randomized Complete Block Design (RCBD) replicated three times giving forty-eight plots. The treatments, their designations and application rates are shown in Table 1.

S/N	Treatments	Designation	Rate (kg/plot)	Rate (t/ha)
T1	Boiler ash	BA ₁₀₀	120	100
T2	Boiler ash	BA ₅₀	60	50
Т3	Boiler ash	BA_{10}	12	10
T4	Poultry droppings	PM ₂₀	24	20
T5	Poultry droppings	PM_{10}	12	10
T6	Poultry droppings	PM ₅	6	5
T7	N.P.K 20: 10: 10	NPK ₃₀₀	0.36	0.3
T8	N.P.K 20: 10: 10	NPK150	0.18	0.15
T9	N.P.K 20: 10: 10	NPK ₇₅	0.09	0.075
T10	Boiler ash + poultry droppings	$BA_{100} + PM_5 \\$	120 + 6=126	100 + 5 = 105
T11	Boiler ash + poultry droppings	$BA_{50}+PM_{10}$	60 + 12=72	50 +10= 60
T12	Boiler ash + poultry droppings	$BA_{10}+PM_{20}$	12 + 24=36	10 + 20=30
T13	Boiler ash + NPK 20: 10: 10	$BA_{100} + NPK_{75}$	120+0.09=120.09	100+0.075=100.075
T14	Boiler ash + NPK 20: 10:10	$BA_{50} + NPK_{150}$	60 + 0.18 = 60.18	50 +0.15=50.15
T15	Boiler ash + NPK 20: 10: 10	$BA_{10} + NPK_{300}$	12 + 0.36= 12.36	10 +0.3 =10.3
T16	Control	Control	No amendment	No amendment

 Table 1: Treatments applied, their designations and application rates.

3.9. Application of Soil Amendments

The boiler ash, poultry droppings and their mixtures were broadcast and evenly distributed with rake and then incorporated into the soil with hoe two weeks before planting, while inorganic fertilizer was applied by ring method four weeks after sowing.

3.10. Planting

Prior to planting, a pre-emergence herbicide (Primextra) was applied two days before the desired planting date at the rate of 5 litres per hectare. Planting was done in mid-May 2013. Two seeds of maize (*Zea mays* L.) Var. Oba super 11) were sown per hole using interrow and intra row spacing of 0.75m by 0.25m on each of the 4m by 3m plots. Plants were later thinned down to one per stand- two weeks after planting, thus giving a plant population of about 53,333 plants per hectare and 64 plants per plot. Supplying was done during thinning where necessary.

3.11. Cultural Practices

Weeding was manually carried out four weeks after planting. Furadan was applied at 4 and 8 weeks after planting to control stem borer and termites.

3.12. Data Collection

3.12.1. Measurement of Growth Characteristics

3.12.1.1. Germination percentage

The number of emergent seedlings was counted daily from four days after sowing (DAS), and germination was considered complete on any given plot once there was no further increase in the number of seedlings.

Germination percentage =Number of seeds germinated / Number of seeds sown \times 100

The relative seed germination % (RSG) was calculated thus:

RSG= Number of seed germinated in treated plot/ No of seeds germinated in control plot.

3.12.1.2. Plant height

Five plants were randomly sampled from two rows at the centre of each plot and tagged. The plant height was measured to the nearest centimeter (cm) from the base of the plant to the base of the unopened apical leaf at 4, 6, 8 and 10 WAP. The mean height from the 5 randomly selected plants from the middle rows was taken as the score for each plot.

3.12.1.3. Stem diameter (cm)

Stem diameter was measured at the first nodal point at the base of the earlier five randomly selected and tagged plants, and used to compute the mean stem diameter score for each plot at 4, 6, 8 and 10 weeks after planting.

3.12.1.4. Number of leaves per plant

The number of fully opened, mature and non-senescent leaves was counted for each of the earlier five randomly selected and tagged plants, and was used to compute the score for each plot at 4, 8 and 10 WAP.

3.12.1.5. Leaf area index (LAI)

In order to estimate LAI, the leaf area was determined with a meter rule by taking measurements of the length and breadth of leaves taken from the bottom and middle of the earlier five randomly selected and tagged plants, average is taken and product multiplied. From the leaf area measured; leaf area index (LAI) was determined using the relationship below by Shortall and Liebhardt (1975).

 $LAI = Y \times N \times AL \times (AP)^{-1}$

Where Y= population of plants per plot

N= Average number of leaves

AL= Average area per leaf

AP= Area of plot

3.12.1.6. Shoot biomass (dry matter) yield per plant (g)

At 4 weeks after planting (WAP), two randomly selected and destructively sampled (up rooted) plants from the middle rows were used as score for each plot. The roots were cut off at the base of the shoot and later dried in an oven at 60°C over 48 hours before being weighed to obtain dry weight. This procedure was repeated at 8 WAP and later at harvest (12WAP).

Plant growth rate (PGR) and relative growth rate (RGR) were calculated as given by Hunt (1990), but implemented using heat units expressed as growing degree days (°Cd) (Yunusa and Gworgwor, 1991)

 $PGR = \hat{e} wd/\hat{e} H \tag{1}$

 $RGR = (\hat{e} \text{ wd/ } \hat{e} \text{ H})/\text{ Wdi} \qquad (2),$

in which ê wd is the change in dry weight per plant, wd is the initial plant dry weight (i.e., at 4WAP) and H is the temperature index taken as sums of mean daily temperatures between the two dates. The RGR is often described as the compound interest in growth (Hunt, 1990).and accounts for pre-existing weight in assessing subsequent increments. This enables us take into account any earlier influence of fly ash on plant weight between emergence and the first sampling at 4WAP.

3.12.2. Measurement of Yield and Yield Components

The maize was harvested at 12 WAP and the following parameters were determined:

3.12.2.1. Fresh cob weight (g)

The fresh weight of the cobs obtained from the earlier five randomly selected and tagged plants were measured to the nearest gram and the mean weight was used to compute the score for each plot.

3.12.2.2. Grain yield /plot

The cobs obtained from the five randomly selected and tagged plants were carefully harvested and threshed. The grains were oven-dried to 14 % moisture content and weighed. The grain yield in tons per hectare based on the plant population of 53,333 plants / hectare used in this study was estimated as per the relationship below:

GYha = Yp x Pha

where,

GYha = Grain yield per hectare

Yp = Average grain yield per plant

Pha = Plant population per hectare

3.12.2.3 .Weight of 100 seeds (g)

One hundred (100) seeds, oven-dried to 14 % moisture content were collected in triplicate from the grains of the five randomly selected and tagged plants and weighed to the nearest gram. Their mean weight was used to compute the score for each plot.

3.12.2.4. Harvest index

Harvest index = economic yield/ biological yield Where, Economic yield =Grain yield/plot

Biological yield = Shoot biomass (dry matter) yield per plot

3.12.2.5. Sustainable yield index (SYI) and Agronomic efficiency (A E)

The sustainability indices (sustainable yield index (SYI) and agronomic efficiency (AE) were also calculated. The quantitative assessment of the sustainability of agricultural practices was developed by Singh *et al.* (1990). Agronomic efficiency was developed by Novea and Loomis (1981). The SYI and AE were calculated as follows:

 $SYI = (Y_m - Sd)/Ymax$

And,

 $AE = (Y_1 \circ Y_o) / F_0$

Where Ym = Mean Yield

Sd = Standard deviation

Ymax = Maximum yield obtained under a set of management practice.

 Y_1 = Grain yield in treated soil in each phase of the study

 $Y_o =$ Grain yield in control plot

 F_o = Amount of nitrogen applied expressed in the same unit

Low values of standard deviation suggest the sustainability of the system (Bhattacharayya *et al.*, 2008).

The field experiment was repeated by the second season in May 2014 without application of amendments to determine their residual effects.

3.12.2.6. Percentage yield reduction (YR)

Percentage yield reduction (YR) with time was computed as

 $YR = (Y_1 - Y_2)/Y_1 \times 100$

Where:

 Y_1 = average maize grain yield (g) in season 1

 Y_2 = average maize grain yield in season 2.

Bio-concentration factor for Bo, Cd and Zn was calculated in grains as

BCF (grains)=C grain/C soil

Where,

C = concentration of a particular metal in ppm

Nutrient uptake was calculated by method of Ombo (1995) as

Nutrient uptake = % nutrient content multiplied by sample dry weight.

Statistical analysis

The data collected were subjected to analysis of variance (ANOVA) using GENSAT Discovery Version (GENSTAT 2009). Differences between means of treatments were compared using the Fisherøs Least Significant Difference (F- LSD) at 5% probability. The theoretical analysis of variance (ANOVA) table for the analysis of the data collected is shown in Table 2.

Source of Variation	Degree of Freedom	Sum of Squares	Mean Square	F Ratio
Replication	r- 1 =3-1=2	RSS	RMS	RMS/EMS
Treatment	t- 1 =16-1=15	TSS	TMS	TMS/EMS
Error	(r-1) (t-1) (2)(15)=30	ESS	EMS	-
Total	rt -1= 48-1=47	Total SS	-	

 Table 2: Theoretical analysis of variance (ANOVA) Table for the analysis of the data

collected.

RSS =Replication Sum of Square, TSS = Treatment Sum of Square, ESS =ErrorSum of Square, RMS=Replication Mean Square, TMS=TreatmentMean Square, EMS=Error Mean Square.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1. Physico-Chemical Properties of the Soil Prior to Treatment Application

4.1.1. Soil Physical Properties Prior to Treatment Application

The soil physical properties of the experimental site prior to treatment application are shown in Table 3. The soil was sandy clay loam in texture with bulk density value of 1.98Mgm⁻³. It was characterized by moderately rapid saturated hydraulic conductivity (10.14cmhr⁻¹) and a total porosity of 48%, indicating high rate of water infiltration into the soil, a situation which would encourage leaching of plant nutrients. The low value of soil water holding capacity (24.4%) of the site coupled with low value of mean weight diameter (MWD) of 0.53 implied that the site was physically degraded and required amelioration for sustainable crop production. This observation is typical of the general status of most soils of southeastern Nigeria (Ano and Agwu, 2005).

Soil properties	Unit	Value		
Coarse sand	gkg ⁻¹	380		
Fine sand	gkg ⁻¹	290		
Silt	gkg ⁻¹	110		
Clay	gkg ⁻¹	220		
Textural class		Sandy clay loam		
Bulk density	Mgm ⁻³	1.98		
Total porosity	%	48		
Saturated hydraulic				
conductivity	cm/hr.	10.14		
Mean weight diameter		0.53		
Water holding capacity	%	24.4		

Table 3: Initial soil physical properties of the study location

4.1.2. Soil chemical properties prior to treatment application.

Data summarizing the chemical properties of the experimental soil used for the study are shown in Table 4. The soil was very strongly acidic with pH 4.8. Such pH condition of the soil could be attributed to the high rainfall peculiarity of the area coupled with the high sand proportion of the soil. This implies that basic cations such as Ca⁺, K⁺, Na⁺ and Mg²⁺ would be leached more easily as texture determine the degree of retention or ease of leaching of basic cations. Soil exchangeable K, Na, Ca, and Mg were low, indicating poor soil fertility. This result agrees with the findings by Nwite et al. (2011) and Akinmutin (2014) who observed that Ultisols of southeastern Nigeria are low in exchangeable calcium, potassium and magnesium. The organic carbon content was moderate (1.29 mg kg⁻¹), and may be ascribed to the long-term grass fallow of the site. Total nitrogen was moderate $(0.23 \text{ mg kg}^{-1})$ but available phosphorous (7.46 Mg kg⁻¹) and potassium (0.18 cmolkg⁻¹) were low (FAO, 2004). The Ca and Mg contents of 0.80 and 1.0 cmol kg⁻¹ respectively was below 10 mg and 3 mg for Ca and Mg respectively soil critical levels for maize in southeastern Nigeria. The exchangeable acidity and C.E.C were 4.4 and 8.4 respectively. The soil extractible micronutrients (Mn, Fe, and Zn) were 0.2, 1.12 and 2.2 mgkg⁻¹ respectively. These values are lower than the established critical levels of 5.00, 1.00 and 3.00 mg kg⁻¹ respectively (Oluwatosin and Ogunkunle, 1991). The soil boron and cadmium concentrations were also low.

The insufficient levels of the major and micronutrients in the soil used for the study suggest that the effect of the treatment on the soil and test crop would be highly manifested.
Soil properties	Unit	Value
pH (H ₂ 0)		4.8
Organic carbon	$mg kg^{-1}$	1.29
Total Nitrogen	$mg kg^{-1}$	0.238
Available P	mg kg ⁻¹	7.46
Exchangeable cations		
Ca ²⁺	cmolkg ⁻¹	0.80
Mg^{2+}	cmolkg ⁻¹	1.00
\mathbf{K}^+	cmolkg ⁻¹	0.185
Na^+	cmolkg ⁻¹	0.364
Extractible micronutrients and	l heavy metals	
Mn	$mg kg^{-1}$	0.2
Fe	$mg kg^{-1}$	1.12
Zn	$mg kg^{-1}$	2.2
Во	mg kg ⁻¹	0.59
Pd	mg kg ⁻¹	n.d.
Cd	mg kg ⁻¹	7.5

Table 4: Initial soil chemical properties of the study location

n.d.= not detectable.

4.2. Metrological Data of the Experimental Site

Some metrological data of the experimental site during the growing season (April-August) in 2013 and 2014 as recorded by National Space Research and Development Agency - Centre for Basic Space Science Nsukka are shown in Figures 1, 2 and 3. The total precipitation obtained during the cropping season (April-August) of 2013 was 856mm, with a monthly average of 171mm. In 2014, the total precipitation was 561mm with a monthly average of 112mm. The average monthly precipitation was 14% higher in 2013 and 25% lower in 2014 than the long - term monthly average of 141.7mm. In 2013, total precipitation was higher than that of 2014 by 295mm and better distributed. This may have contributed to the higher growth and yield of maize in 2013 than 2014. The average monthly temperature ranged from 23 and 24°C in August to 27°C in April of 2013 and 2014 respectively. The average temperature was similar to the long term-year average range (21- 31°C) for the area. The relative humidity ranged from 73% in April of both years to 83% and 78% in August of 2013 and 2014 respectively. Generally, differences in amount and distribution of moisture may have influenced the study with respect to cropping.





Fig.2. Mean monthly air temperature(oC) of the experimental site during the cropping period.



4.3. Agronomic Potentials of the Boiler Ash and Poultry droppings

4.3.1. Physical properties of the boiler ash and poultry droppings

The physical properties of boiler ash (BA) obtained from burning Oil palm mill wastes at Solive Vegetable Oil Mills Ltd Nsukka and poultry droppings (PM) are shown in Table 5. The BA consisted mostly of sand-sized particles (701gkg⁻¹) with about 86 and 31 gkg⁻¹ of silt and clay-sized fractions, respectively. It had a saturated moisture content of 76.9 % and a density of 0.374 Mgm⁻³, as determined by the self ócompacting method (Brasil, 2007). The PM consisted of coarse fractions of the litter materials and fine particles of the fecal droppings, and a saturated moisture content of 36.9% with density value of 0.49 Mgm⁻³. The mineral fertilizer was in granulated form.

The particle size of fertilizer materials directly affects release rate, potency, and working hazards such as dust generation (HORIBA, 2016). Approximately 12% of the oil palm boiler ash (OPBA) used in this study was made up of silt and clay-sized fractions contrary to that obtained from burning bituminous coal, wood and paper mill ashes, which were 58,65 and 69% respectively (Etiegni, 1991, Kalra et al. (1997, Chirenge and Ma, 2002, Mladenov *et al*, 2011). The predominance of sand-sized particles in the ash is likely to offer a good degree of pore space suitable for drainage, aeration of soils and root penetration. Its addition in the soil changes the physical properties such as texture, bulk density, water holding capacity, hydraulic conductivity and particle size distribution (Shama *et al.*, 2002). The expected decrease in bulk density of the soil may in turn improve its porosity and better workability and enhance water retention capacity (Page et al., 1979). The oil palm boiler ash (OPBA) having coarser fractions than PM, is likely to impart greater influence on the soil pore system and aggregate stability. This is because surface texture of ashes significantly affects its frictional characteristics and stability (Huang, 1990) and coarse textured ashes experience higher friction and stability. Coarse fractions of ash are less reactive to the environment (Larsson and Westling, 1998) therefore; the coarse gradations of the ash can render it less reactive (Rifad, 2009) than the poultry droppings. Agronomically, PM may exhibit both coarse and fine textured characteristics and as such may be superior in nutrient release.

The density of BA (0.374 Mgm⁻³) obtained from burning oil palm wastes was very low compared to that of bituminous coa l(0.93 Mgm⁻³), paper mill ash (1.01 Mgm⁻³) or bagasse ash (1.95 Mgm⁻³) (Etiegni, 1991; Chirenge and Ma, 2002; Aigbodion et al. 2010; Mladenov et al, 2011). It is about 6% lighter than the poultry droppings. In comparison to the

		Boiler ash		Poultry drop	ppings
Particle size	Unit	Mean	Standard	Mean	Standard
		Value	Deviation	Value	Deviation
>2.00mm	(gkg ⁻¹)	182	7.289	-	-
2.00-1.00mm	(gkg ⁻¹)	347	13.88	-	-
1.0-0.50mm	(gkg ⁻¹)	354	5.806	-	-
0.50-0.25mm	(gkg ⁻¹)	86	3.692	-	-
<0.25mm	(gkg ⁻¹)	31	0.516	-	-
S.M.C.	(%)	76.90	1.097	36	0.86I
Bulk density	(Mgm^{-3})	0.37	0.025	0.49	0.029

Table 5: Particle size,	Bulk density and Saturation moisture content (S.M.C) of t	the
boiler ash and	poultry droppings (Number of samples = 3)	

poultry droppings, its lower bulk density is likely to increase the potential for dust formation, which may create problem in its transportation and storage in dry condition.

The saturation moisture content of the OPBA (77 % on weight basis) was very high compared to that of paper mill and bituminous coal ashes that were 56.9 and 59.3%, respectively (Etiegni, 1991; Serafimova et al. 2011). Its higher saturation moisture content was also in conformity with the findings by Huang (1990) who reported that water adsorption values of boiler ash vary considerably depending on porosity and surface texture of the ash. Porous surface textured BA generally shows higher adsorption values. It held more water than poultry droppings probabily due to its coarse texture and high porosity.

4.3.2. Chemical properties of the boiler ash and poultry droppings

The chemical properties of the boiler ash and poultry droppings are shown in Table 6. They are strongly alkaline as shown by their pH values of 9.2 and 8.3, respectively. Boiler ash obtained from burning oil palm mill wastes had a calcium carbonate equivalence of 35.7% while that of PM was 21.3%. Organic carbon (12.4 mg kg⁻¹) and total nitrogen (0.20 mg kg⁻¹) contents of the ash was lower than that of the poultry droppings (43.17 mg kg⁻¹) and (4.20 mg kg⁻¹), respectively. The phosphorus content of the boiler ash (293.8 mg kg⁻¹) was about 40 times higher than that of the poultry droppings (8.32 mg kg⁻¹). The NPK plant nutrient ratios of the BA,PM and NPK mineral fertilizer were 1-147-5, 25-5-1, 20-10-10 respectively. The concentration of Mg²⁺ (7.2 Cmolkg⁻¹) and K⁺ (10.56 Cmolkg⁻¹) were higher in the ash than in the poultry dropping which were - Mg²⁺ (4.77 Cmolkg⁻¹) and K⁺ (6.7 Cmolkg⁻¹). C: N ratio of the BA and PM were 62 and 10 respectively. The ratio of Ca: P was 24 and 0.2 whereas Ca: Mg was 4.8 and 1.42 for BA, and PM, respectively.

The oil palm boiler ash (OPBA) had lower pH value than most ashes reported in literature (Etiegni, 1991; Chirenge and Ma, 2002; Serafimova *et al.*, 2011; Schiemenz *et al.*, 2011) except that obtained from coal (Katiyar *et al.* 2012). This implies that it has lower liming potentials than most of the ashes and a less concern for the problems of excessive alkalinity when used as a soil improver. The high pH of the ash is consistent with the occurrence of basic metal salts, oxides, hydroxides and/or carbonates. In comparison with the poultry droppings, the ash will most likely modify the soil pH when applied since it may have little or no organic acids. The strong alkalinity indicates that the boiler ash could be an alternative to lime, either by itself or as a mixture of lime and ash. The pH value of the BA clearly defines its high potential as a raw material resource for the improvement of acidic

Properties	Units	Boiler ash	Standard	Poultry	Standard
			Deviation	droppings	Deviation
pH (H ₂ 0)		9.2	0.252	8.3	0.252
Organic carbon	mg kg⁻¹	12.4	0.438	43.1	3.339
Nitrogen	mg kg⁻¹	0.20	0.035	4.15	0.189
Phosphorus	mgkg ⁻¹	293.8	20.89	8.32	0.87
Potassium	Cmolkg ⁻¹	10.56	0.862	1.7	0.515
Calcium	Cmolkg ⁻¹	1.50	0.265	4.77	0.395
Magnesium	Cmolkg ⁻¹	7.2	0.764	6.77	0.451
C : N ratio		62		10	
C: P ratio		24		0.20	
Ca : Mg ratio		4.8		1.42	
Soluble sodium	Cmolkg ⁻¹	599.7	9.292	1.20	0.258
Cl	mgkg ⁻¹	39.7	1.212	n.d	
CO ₃ ⁻	mgkg ⁻¹	1.43	0.252	n.d	
HCO ₃	mgkg ⁻¹	16.6	2.724	n.d	
SO4 ²⁻	mgkg ⁻¹	62.9	6.346	n.d	
CaCO ₃ equivalence	%	35.7		21.3	
Electrical conductivity	d/s/cm	433.8	18.26		

Table 6: Chemical properties of boiler ash and poultry droppings (3 Samples)

n.d =Not determined, C= Carbon, N= Nitrogen, P= Potassium, Ca =Calcium, Mg = Magnesium, Cl- =Chloride, CO_3 = Carbonate, HCO_3 = Hydrogen carbonate, SO_4^{2-} = Sulphate

soils (Van herck and Vandacastleele, 2001). Therefore, application of the BA to Ultisol may enable farmers to grow a much wider range of crops more cost efficiently.

The acid neutralizing value (NV) measured, as calcium carbonate equivalence is one of the important indices in evaluating the liming effect value of ash in relation to its use in agriculture. According to Saarsalami (2001), capacity of a liming agent to neutralize soil acidity depends on the levels of soluble and hydrolysable bases such as oxides, hydroxides, carbonates and silicates. Cations such as Ca^{2+} , Mg^{2+} and K^+ are the interactive ions. According to the NV, the BA has high potentials as a liming agent to neutralize soil acidity and act as a soil amendment agent. Therefore, the ash has a higher potential as a liming agent and / or for the release of these nutrients to the soil.

The low content of organic carbon in the ash could be attributed to loss of carbon during combustion of the biomass in the boilers. Therefore, the addition of the ash in soil at low doses may not significantly influence the soil organic matter content compared to the poultry droppings. However, the prescribed reduction of carbon in high carbon materials (Gomez-Bare *et al.*, 2009), before field application to minimize nitrogen immobilization, which may be cost and resource prohibitive may not be required in agronomic utilization of this ash.

The poultry droppings had the highest levels of total N, total P and narrowest ratios of C: N and C: P, suggesting superior mineralization of organic forms of N and P compared to the BA. The low nitrogen content of the ash could be attributed to the volatile nature of the element under combustion (Singh and Yunus 2000). Agronomically, the insufficient nitrogen in the ash is a remarkable constraint to its utilization as a nitrogen fertilizer source. The C: N ratio of the ash was above 20, indicating N content of less than about 2.5%, which according to Stevenson and Cole (1999) may lead to decrease in soil mineral nitrogen level.

Several reasons such as high phosphate potentials of the oil palm mill wastes and /or the combustion conditions may have been responsible for the high phosphorus content of the ash. It is expected that the boiler ash would be superior to the poultry droppings in the supply of phosphorus to plants. Unfortunately, this P is not readily available to plants, which may be due to its active interaction with Al, Fe and Ca present in alkaline BA (Schiemenz and Eichler-Tobermann, 2010; Gupta *et al.* 2012). In contrary, Obernberger (1997) noted that higher P availability could be expected from agricultural biomass ashes such as bagasse ash than from wooden biomass ashes. Therefore, the phosphorus content of this ash should be considered a critical factor in determining its application rate to avoid problems associated with excessive P in soil. Many researchers documented that organic P forms in animal manures are not readily available for plant uptake as they have to be mineralized into inorganic forms in the soil .Their concentration are highly dependent on the Ca:P ratio in manures. When the total Ca:P ratio is higher, there is a net transformation of more soluble (dicalcium phosphate) to less soluble P compounds (hydroxylapatite) as reported by Nair *et al.* (2003) and Toor *et al.* (2005).

Consistent with the high pH values, the ash had higher concentrations of potassium (10.56 Cmolkg⁻¹) and magnesium (7.2 Cmol kg⁻¹) and low in calcium (1.2 Cmol kg⁻¹). The concentrations of K and Mg were higher in the ash than in the poultry droppings, which were (1.7 Cmol kg⁻¹), and (6.77 Cmol kg⁻¹), respectively. The presence of large quantities of sodium and potassium salts may have given the ash its high pH (Huang *et al.*, 1992). The Mg concentration of both amendments was high indicating that both have high fertilizing potentials. These values are low [Appendix IV (a)] for profitable crop production and as such auxiliary calcium source may be required when they are used as fertilizer (FAO, 1979).

The calcium concentration of the boiler ash (1.5Cmolkg⁻¹) and poultry droppings (4.77 Cmolkg⁻¹) were below the minimum limits value of 6% for Ca in soils of southeastern Nigeria (FAO, 1979). Therefore, these residues may require supplementary calcium source to be used as fertilizer. Generally, the low levels of nitrogen (0.20 mg kg⁻¹), calcium (1.5 Cmolkg⁻¹) and organic carbon (12.4 mg kg⁻¹) of the ash mark it as a nutritive deficient substrate.

4.3.3. Micronutriet and Heavy Metal Concentrations in the Boiler ash and Poultry droppings

In addition to the presence of beneficial nutrient elements, the concentrations of heavy metals (metalloids) must be taken into account when ashes are considered for use as soil amendment. Table 7 shows the content of Mn, Zn, Fe, Bo, Pd and Cd in the BA and PM. Manganese content of the BA (17.5 mgkg⁻¹) was 22 times higher than that of the PM (0.92 mgkg⁻¹) and 4 times higher in Zn. However, the Fe content of the PM (167 mgkg⁻¹) was 31 times higher than that of the BA (16.09 mgkg⁻¹).The cadmium content of the BA and PM were 16.71 and 29.27 mgkg⁻¹ respectively, while, their lead content was below detection.

High Cd content in soils may pose many environmental and health concerns due to its ability to bio-accumulate within plant, animal and human tissues (Grant *et al.*, 1998). Application of PM has a higher potential to increase the pool of Cd within the soil than the

Element	Unit	Boiler ash	Standard	Poultry	Standard
			deviation	droppings	deviation
Mn	mgkg ⁻¹	17.50	0.953	0.92	0.106
Zn	mgkg ⁻¹	19.37	0.676	5.57	0.862
Fe	mgkg ⁻¹	16.09	0.737	167.0	4.082
В	mgkg ⁻¹	31.51	0.091	0.382	0.025
Pd	mgkg ⁻¹	trace	-	Trace	-
Cd	mgkg ⁻¹	2.6	0.819	29.79	2.295

Table 7: Micronutrient and heavy metal content of the boiler ash and poultry droppings

Mn = Manganese, Zn = Zinc, Fe = Iron, B =Boron, Pd = Lead, Cd = Cadmium

BA. This is because BA contains less Cd and high pH, which could increase soil pH thereby reducing Cd availability to plants. Generally, the boiler ash was higher in Mn and boron, and medium in Fe than that of PM. The high concentration of these elements in the ash may pose as potential toxicants when applied under high rates, since, boron and potassium content and alkalinity of ashes have been implicated in the phyto-toxicity of ashes when applied at high application rates (Etiegini *et al.*, 1990).

It is very low in zinc but high in manganese. The lead content of OPBA was below detection and boron was very low but Cd was very high. In comparison with other ashes, the only heavy metal that shows concern is Cd, however, there has not been any published report of metals contained in wood ash constituting a risk to environment or crop production.

From the above comparison, the OPBA produced by Solive Vegetable Oil Mills Ltd Nsukka used in this study has similar characteristics to ashes used by several authors and should benefit crop production by acting as a soil conditioner as well as fertilizer.

The total concentration of major and trace elements in the boiler ash sample may be informative as to the presence of nutrients or potentially hazardous heavy metal contaminants but provide little indication of their bioavailability, mobility and other essential properties related to their true environmental and ecological impacts (Ahnstrom and Parker, 1999). Therefore, there is the need to assess their impact on soil and crop productivity

4.4. Treatment Effect on Soil Physical Properties 4.4.1. Particle size distribution

The result of the particle size distribution following the application of the various amendments is presented in Table 8. The result indicates that application of high rates of boiler ash (BA₁₀₀, BA₅₀) significantly (p<0.01), altered the mechanical composition of the amended soil after the first cropping season. Sand and clay fractions were apparently unaltered while the silt component differed significantly (p<0.01) among the treatments. The surface texture of the soil changed from sandy clay loam to sandy loam by the apparent increase in silt ó sized particles. This change is surprising and difficult to explain. It is however, possible that the boiler ash particles stabilized as silt - sized particles, which could not be disaggregated by the dispersing agent used in normal particle size analysis. Attempt will be made to separate silt from silt- sized boiler ash particles in subsequent research. The spurious alteration of the surface texture from sandy clay loam to sandy loam at the end of

			First cropping season			Second cropping season			eason	
Treatment	C.S	F.S	Silt	Clay	Texture	C.S	F.S	Silt	Clay	Texture
		g	kg⁻¹				gk	kg ⁻¹		
BA ₁₀₀	465	255	100	180	SL	415	335	100	150	SL
BA ₅₀	465	255	100	180	SL	425	325	100	150	SL
BA_{10}	405	315	60	220	SCL	425	285	70	220	SCL
PM ₂₀	365	345	60	230	SCL	415	295	70	220.	SCL
PM_{10}	435	285	60	220	SCL	420	300	60	220	SCL
PM_5	410	280	60	220	SCL	405	295	80	220	SCL
NPK300	290	440	50	220	SCL	400	300	80	220	SCL
NPK ₁₅₀	375	355	50	220	SCL	425	285	70	220	SCL
NPK ₇₅	420	310	50	220	SCL	400	350	70	180	SL
$BA_{100} + PM_5$	420	310	50	220	SCL	425	325	110	140	SL
BA50 +PM10	405	325	70	200	SL	410	330	90	170	SL
$BA_{10} + PM_{20}$	375	355	70	200	SL	425	305	90	180	SL
BA100+NPK75	390	330	70	200	SL	410	340	110	140	SL
BA50+NPK150	350	370	80	200	SL	405	335	140	150	SL
BA10+NPK300	375	335	60	230	SCL	415	325	80	180	SL
No amendment	405	315	60	220	SCL	400	310	80	210	SCL
F-LSD _{0.5}	N.S	N.S	28.8	21		N.S	36.8	N.S	50.2	

Table 8: Particle size distributions as as influenced by different rates and combinations of boiler ash, poultry droppings and NPK 20:10:10

C.S= Coarse sand, F.S = Fine sand, F-LSD_{0.5}= Fishers least significant difference at 5% level of probability. N.S =Non- significant, SCL= Sandy Clay Loam, SL=Sandy Loam

the second cropping was also possibly induced by significant differences in the fine sand and clay fractions. The effect of applying BA_{100} and BA_{50} treatments were consistent at the end of the second cropping season.

The boiler ash due to its coarse texture and slight resistance to degradation may have become a significant component of the soil matrix and altered the particle size distribution. Ghodrati (1995) observed a similar result where application of fly ash from coal material to sandy soil permanently altered the soil texture, increased micro porosity and improved water holding capacity of the soil. Similarly, Jones and Amos (1976), Basil *et al.* (2001) and Gray *et al.* (2003) observed that high rates of boiler ash from sugar cane bagasse changed the surface texture of soil from sandy clay loam to sandy loam by increasing the silt content of the soil. The result obtained at the end of the first cropping season also agrees with the findings of Oku *et al.*; (2010); Phil-Eze, (2010) and Obalum et al.; (2013) that silt contents exhibit highest variability among the other soil fractions.

4.4.2. Bulk Density and Porosity

The soil bulk density, total and macro porosity were significantly (p<0.01) influenced by the application of the various amendments (Table 9). At the end of the first cropping season, the 300 kgha⁻¹ NPK (NPK₃₀₀) treatment recorded the highest bulk density (1.76 Mgm⁻³) among all the amended plots with BA_{100} having the least value (1.03 Mgm⁻³). The bulk density value (1.92 Mgm⁻³) of the control plot was generally higher than the value obtained in any of the amended plots. Sole boiler ash and poultry dropping treatments decreased the bulk density in line with their application rates. Blending 100tha⁻¹ boiler ash with 75kg NPK (BA₁₀₀ + NPK₇₅) increased the bulk density significantly (p<0.01) by about 28% relative to sole boiler ash application. Comparatively, the capacity of 50 tha⁻¹ boiler ash in reducing the soil bulk density was statistically the same (p<0.01) with that of 10 tha⁻¹ poultry droppings. At the end of the second cropping season, the bulk density varied slightly among the various amended plots. The least bulk density (0.88 Mgm-3) was obtained in the plots amended with $BA_{100} + PM_5$ while the control had the highest value (1.55 Mgm⁻³). The other treatments maintained their first cropping season trend. The bulk density values obtained at the first cropping season evaluation was higher than that of the second cropping. Ahmad et al. (2007) who attributed it to field variation made a similar observation.

The total porosity of the soil was significantly (P<0.01) influenced by the type and quantity of the soil amendment used. At the end of the first cropping season, the total

	Bulk density((Mgm ⁻³)	Total Porc	osity (%)	Macro por	osity (%)
Treatment	1 st C.S	2 nd C.S	1 st C.S	2 nd C.S	1 st C.S	2 nd C.S
BA ₁₀₀	1.03	1.02	61	62	13	9
BA ₅₀	1.22	1.08	54	59	13	10
BA ₁₀	1.57	1.23	41	54	13	7
PM_{20}	1.22	1.03	54	61	14	7
PM_{10}	1.30	1.12	51	58	14	4
PM ₅	1.44	1.18	46	56	10	9
NPK ₃₀₀	1.76	1.28	34	52	19	7
NPK150	1.57	1.27	41	52	9	7
NPK ₇₅	1.56	1.23	41	54	14	9
$BA_{100} + PM_5$	1.04	0.88	61	67	14	7
$BA_{50} + PM_{10}$	1.25	1.17	53	56	13	8
$BA_{10} + PM_{20}$	1.32	1.23	50	54	13	8
$BA_{100} + NPK_{75}$	1.23	1.11	54	56	14	7
$BA_{50} + NPK_{150}$	1.45	1.21	45	54	14	12
$BA_{10} + NPK_{300}$	1.71	1.27	36	52	18	7
No amendment	1.92	1.55	28	42	12	8
F-LSD(0.05)	0.094	0.027	2.70	1.19	1.43	n.s

 Table 9:
 Soil bulk density and porosity as influenced by different rates and combinations of boiler ash, poultry droppings and NPK 20:10:10

1st C.S= First cropping season, 2nd C.S = second cropping season, n.s= non-significant at p<0.05, F-LSD_{0.05}= Fishers least significant difference at 5% level of probability.

porosity of the soil increased from < 28 % in the control plot to > 61% in the BA₁₀₀ plot. In the second cropping season, total porosity increased in the control plot from 28 to 42% representing an increase of 51%. While in the BA₁₀₀ + PM₅ which had the highest value, the change was only about 10%. The macro porosity of the soil following the different amendments ranged from 9% in NPK₁₅₀ amended plots to 19% in NPK₃₀₀ treated plots. There was no significant residual effect of all the amendments on macro porosity of the soil.

The result of the total porosity followed a similar trend with that of the bulk density. This may be ascribed to the improvement of the soil structure by increased soil granulation and improved soil porosity.

These changes in bulk density, total and macro porosity of the top soil (0-20cm) as affected by the treatments might have been due to direct pore contribution from the pores within the BA or PM. It may as well be due to creation of packing or accommodation pores, and / or improved aggregate stability, which leads to the modification in the macro and micro-

pore size distribution of the soil. The amendment therefore, repackaged the soil leading to lower soil density per unit volume. These results are in conformity with the findings of Kalra *et al.* (1997); Prabakar *et al.* (2004) and Kohli and Goyal, (2010) in fly ash amended soils.

The reduction in the bulk density of the soil may also have been because of the lower bulk density and higher organic matter content of the boiler ash and poultry droppings respectively as compared to the bulk density of the soil. The decrease in bulk density could also be because of increased microbial activity associated with increased nutrient availability at that rate which could lead to pulverization of the soil and possible movement of heavy clay particles down the soil column. The large porosity may also be related to the presence of numerous macro pores that results from both faunal activity and root development.

4.4.3. Soil Water Characteristics

The dynamics of soil moisture regime as affected by the amendments is shown in Table 10. There were significant differences (p<0.01) in gravimetric moisture content (WHC) among the treatments at the end of both cropping seasons. Application of BA₁₀₀ increased the water holding capacity of the soil significantly (p<0.01) from 39% in the control plot to 54% at the first cropping season while WHC increased to 49 and 46% in PM₂₀ and NPK₃₀₀ treated plots respectively. The residual effect of BA₁₀₀ increased the WHC to 68% while in PM₂₀ and NPK₃₀₀ treated plots it decreased to 42 and 40% respectively. The residual effects of the boiler ash treatments were higher at both BA₅₀ and BA₁₀₀ levels. Blending them with either poultry droppings or NPK fertilizer

	WHC (%)		WHC (60	_{cm)} (%)	SHC (cm	hr ⁻¹)
Treatment	1 st C.S	2 nd C.S	1 st C.S	2 nd C.S	1 st C.S	2 nd C.S
BA ₁₀₀	54	68	44	57	108.7	73.2
BA ₅₀	45	49	32	41	74.7	52.0
BA_{10}	43	36	32	31	41.6	38.4
PM_{20}	49	42	38	35	43.7	40.3
PM_{10}	38	45	32	42	91.6	36.0
PM ₅	30	43	23	35	100.8	54.1
NPK ₃₀₀	46	40	34	34	83.5	60.4
NPK ₁₅₀	42	39	33	34	30.8	24.5
NPK ₇₅	35	42	26	35	32.2	49.8
$BA_{100} + PM_5$	45	53	37	46	58.3	21.0
$BA_{50} + PM_{10}$	41	44	32	36	59.3	83.6
$BA_{10}+PM_{20}$	30	43	23	36	26.0	38.1
$BA_{100} + NPK_{75}$	51	51	39	44	65.4	141.0
$BA_{50} + NPK_{150}$	46	48	36	40	66.0	85.5
$BA_{10} + NPK_{300}$	48	34	37	29	44.2	16.3
No amendment	39	40	30	33	33.5	40.3
F-LSD _{0.05}	0.9	12.7	1.81	1.0	n.s	37.6

Table 10: Soil water retention and saturated hydraulic conductivity as influenced by different rates and combinations of boiler ash, poultry droppings and NPK 20:10:10.

1st C.S= First cropping season, 2nd C.S= Second cropping season WHC=Water

holding capacity at saturation, WHC (60cm) =Moisture content at 60cm tension, SHC=saturated hydraulic conductivity, n.s=non-significant at 5% level of probability, F-LSD_{0.05}= Fishers least significant difference at 5% level of probability. reduced their effectiveness in increasing the water holding capacity of the soil. For instance, the moisture holding capacity of soils treated with $BA_{50} + NPK_{150}$ and $BA_{10} + NPK_{300}$ were significantly lower than the control (31%).

Comparatively, the boiler ash treatments were superior to the poultry droppings and NPK treatments in modifying the water holding capacity of the soil. The superiority of the boiler ash over the poultry droppings may be attributed to the probable presence of hydrophobic organic substances (De Bano, 1969; Fink, 1970) in the poultry droppings treated plots. Little is known about the chemical nature of these hydrophobic substances but it has been shown that microorganisms may produce them; particularly certain fungi (Savage *et al.*1969). The presence of the hydrophobic substances may have formed a water repellant lattice around the soil aggregates.

The moisture content at 60cm tension differed significantly (p<0.01) among the treatments at the end of the first and second cropping seasons Table 10. This trend connotes differences in the magnitude of soil moisture storage within the root zone. At the end of the first cropping season, BA₁₀₀ treated soils held significantly (p<0.01) higher amount of water (44%), followed by PM₂₀ rate (38%). Mean soil moisture content at 60cm tension at the end of the second cropping season was also higher (55%) under BA₁₀₀ treated soil while non-significant variations existed among other treatments. The results indicate that boiler ash application at BA₁₀₀, BA₅₀, and BA₁₀ held 10, 12, and 10% of their water at the macro pores respectively at the end of the first cropping season, while at the end of the second cropping season they were 11, 8 and 5% respectively. The corresponding values for the control soil were 9 and 7% at the end of the first and second cropping seasons respectively.

Consequently, application of the BA may have increased plant available water through direct pore contribution by increasing the proportion of pores between field capacity (30 m) and the permanent wilting point (0.2 m), and to a lesser extent macro pores (pore diameters > 75 m). An inference from this study therefore indicates that, the superiority of high rate of boiler ash in soil water holding capacity was on water held at the capillary pores. Therefore, the application of high rate of boiler ash increases the chances of plant survival under extended water stress in soils. However, Eisenberg *et al.* (1986) observed that the more water held by ash capillary actions did not increase the amount of water available to plants.

The improved water retention and moisture availability in the ash amended soil may be attributed to the fine particle size of the boiler ash as compared to the soil, and to its attendant influence in reducing dry bulk density and improvement in soil porosity. Similarly, the study is in tandem with the findings of Etiegini *et al.* (1991) which noted that ash is essentially

hydrophilic with particle swelling through absorption of water into the pores by capillary action simultaneously with chemical changes through hydration of oxides to form new compounds. This effect could be beneficial and detrimental in soils where ash might be used as an amendment - in clay soils, small pores might easily be clogged by wetted ash, causing decreased aeration but in sandy free draining soils as in this experimental site, this water holding capacity could be very beneficial to plant growth. The finding agrees with that of Aitken and Bell (1985).The soluble calcium of the BA may also have provided congenial atmosphere for the flocculation of the highly dispersed soil particles and the little organic matter content of the soil provides the much needed protective action to stabilize the physical environment improved by the calcium.

4.4.4. Saturated Hydraulic Conductivity

The results presented in Table 10 above shows that, there was non-significant effect of the treatments on saturated hydraulic conductivity of the soils at the end of the first cropping season. However, at the end of the second cropping season, significant differences (p < 0.01) were observed among some treatments. The soil treated with BA₁₀₀ + NPK₇₅ had the highest value (141.0cmhr⁻¹) followed by BA₅₀ + NPK₁₅₀ (85.5cm hr⁻¹) which was statistically the same with BA₁₀₀, PM₅ and BA₅₀ + PM₁₀. The rest of the treatments did not differ significantly with the control (40.3 cm hr⁻¹).

The non-significant effect of the amendments on saturated hydraulic conductivity at the first cropping season indicates that the high sodium ion content of the boiler ash and the colloidal materials in the poultry droppings could not exert enough influence to alter the saturated hydraulic conductivity of the soil. In the second cropping season, the treatment that had significant higher values than the control may have lost a considerable amount of their clay and silt particles and their base ions within the top layer due to excessive leaching as happens in high rainfall tropical zones. From the study, one can infer that the residual effect of blending boiler ash with NPK fertilizer induced higher saturated hydraulic conductivity.

Generally, the saturated hydraulic conductivity values were high. This may have resulted from abundant bio pores and texture coarser than loamy fine sand (Mc Keague *et al.*, 1983). The findings collaborates that of Steponkus (1992) who reported that ash application at 27tha⁻¹ did not result in violation of the ground water. The result of this study shows that the amendments did not influence the internal drainage of the sandy clay loam soil. This however, may have a wide implication on non-point pollution potentials especially the ground water.

4.4.5. Aggregate Size Distribution

The aggregate size distribution as influenced by the soil amendments during the first and second cropping seasons are presented in Tables 11 and 12. At the end of the first cropping season, the treatments manifested significant (p<0.01) effect on only the >2mm aggregate size. The plot amended with $BA_{100} + PM_5$ had the highest value (2.11) but were statistically the same with $BA_{100} + NPK_{75}$ (1.34) and $BA_{10} + NPK_{300}$ (1.95). The least (0.60) was obtained in BA_{10} treated plots, which however did not differ from the control and the rest

of the other treatments. The aggregate size distribution was in the increasing order of magnitude (0.5-0.25mm), <0.25mm, (1-0.5mm), (2-1.0mm) and >2.0mm.

In the subsequent cropping season, the amendments exerted significant influence on all the aggregate sizes except the 2-1mm aggregate. In the >2.00mm aggregate size, BA₁₀ had the least value (0.70) but at par with BA₁₀₀, BA₅₀, PM₅, NPK ₃₀₀, NPK ₁₅₀, NPK ₇₅ and the control (0.89). The PM₂₀ treated plots had the highest value (1.67) but was statistically (p<0.01) the same with the rest of the other treatments. The 1.00-0.50mm aggregate size ranged from 3.72 in the BA₁₀₀ + PM₅ to 10.71 in the BA₅₀ + NPK ₃₀₀ treatments, while the control was 4.42. Blending the BA₅₀ with NPK ₁₅₀ (BA₅₀ + NPK ₁₅₀) increased the 1.00-0.50mm aggregate size by over 170% while, the rest of the treatments were at par with each other. Among the <0.25mm aggregates, the highest value (8.53) was obtained in the plots amended with BA₅₀. It however, did not differ significantly with BA₁₀₀, BA₁₀₀ + PM₅ and BA₁₀₀ + NPK ₇₅. The least value (5.51) was obtained from the plots treated with BA₁₀ + PM₂₀ which did not differ significantly from PM₂₀, PM₁₀, NPK ₃₀₀, NPK ₁₅₀, BA₅₀ + NPK ₁₅₀ and BA₁₀ + NPK₃₀₀.

		Aggi	regate sizes		
Treatment	>2.0mm	2-1mm	1-0.5mm	0.5-0.25mm	<0.25mm
BA ₁₀₀	0.63	1.86	4.04	9.33	9.14
BA_{50}	0.60	2.91	2.70	9.50	9.29
BA_{10}	0.58	1.72	4.86	9.87	7.97
PM_{20}	1.10	2.51	5.62	8.41	7.26
PM_{10}	1.16	2.48	5.23	8.37	7.76
PM ₅	1.02	1.70	4.42	9.42	8.44
NPK ₃₀₀	0.79	1.82	7.23	7.38	7.78
NPK150	0.81	1.88	4.89	9.05	8.37
NPK ₇₅	0.71	1.43	4.70	9.41	8.75
$BA_{100} + PM_5$	2.11	2.57	3.86	7.91	8.55
$BA_{50} + PM_{10}$	1.06	2.17	4.71	9.47	7.59
$BA_{10}+PM_{20}$	0.98	2.10	5.31	9.63	6.97
$BA_{100} + NPK_{75}$	1.34	1.55	4.08	9.34	8.69
$BA_{50} + NPK_{150}$	1.95	1.82	7.35	6.49	7.39
$BA_{10} + NPK_{300}$	0.82	1.95	5.50	9.07	7.66
No amendment	0.73	1.17	4.11	10.63	8.36
F-LSD _{0.05}	0.860	n.s	n.s	n.s	n.s

Table 11:Soil aggregate size distribution as influenced by different rates and
combination of boiler ash, poultry droppings and NPK 20:10:10 during the
first cropping season

1st C.S= First cropping season, 2nd C.S= Second cropping season, n.s= non-significant at 5% level, F-LSD_{0.05}= Fishers least significant difference at 5% level of probability.

Aggregate sizes						
Treatment	>2.0mm	2-1mm	1-0.5mm	0.5-0.25mm	<0.25mm	
BA ₁₀₀	0.91	1.74	4.06	10.40	8.29	
BA_{50}	0.72	1.55	3.96	10.25	8.52	
BA_{10}	0.69	1.72	5.10	10.97	6.52	
PM_{20}	1.67	2.69	5.68	8.81	6.15	
PM_{10}	1.35	3.06	5.63	8.58	6.38	
PM ₅	1.04	1.99	4.93	9.98	7.06	
NPK300	1.01	1.87	7.60	8.84	5.68	
NPK ₁₅₀	1.23	3.15	5.67	8.91	6.04	
NPK ₇₅	1.19	1.92	5.26	10.11	6.52	
$BA_{100} + PM_5$	1.64	2.51	3.72	8.62	8.51	
$BA_{50} + PM_{10}$	1.08	1.98	4.51	10.66	6.77	
$BA_{10} + PM_{20}$	1.55	2.88	5.89	9.18	5.50	
$BA_{100} + NPK_{75}$	1.43	1.87	4.01	9.80	7.89	
$BA_{50} + NPK_{150}$	1.58	1.82	10.71	4.76	6.13	
$BA_{10} + NPK_{300}$	1.41	2.33	5.70	9.72	5.84	
No amendment	0.89	1.95	4.42	10.94	6.80	
F-LSD _{0.05}	0.5575	N.S	2.076	2.617	0.9112	

Table 12: Soil aggregate size distribution as influenced by different rates and combination of boiler ash, poultry droppings and NPK 20:10:10 during the second cropping season

1st C.S= First cropping season, 2nd C.S= Second cropping season, n.s = non-significant at 5% level, $F-LSD_{0.05}$ = Fishers least significant difference at 5% level of probability.

4.4.6. Soil Aggregate Stability

The result of the aggregate stability of the soil as influenced by the different amendments using different aggregation indices are shown in Table 13. Stability of wetted aggregates measured as percent aggregate stability (% AS) differed significantly (p<0.01) among the treatments at the end of the first cropping season. The % AS of the soils following the application of the amendments ranged from 52% in NPK₇₅ to 67% in BA₁₀ +PM₂₀ treated plots. Amending the soil with BA₁₀₀ and BA₁₀ treatments increased the stability of the soil relative to the control by 14 and 2% respectively while; BA₅₀ reduced it by 4%. However, a combined application of the BA₅₀ with NPK ₁₅₀ eliminated the disaggregating properties of the ash and increased the percentage aggregate stability by 15%.

The residual effect showed similar significant (p<0.01) differences. Soil amended with higher doses of boiler ash (BA₁₀₀, BA₅₀) had significantly (p<0.01) lower stability (51%) than the control (58%). The BA₁₀ treated plots on the other hand increased the stability of the soil from 64 to 69%. The BA₅₀ + NPK ₁₅₀ still maintained the highest aggregate stability status (61%) at the end of the second cropping season.

Percent state of aggregation index (Table 13) also detected significant (p<0.01) influence of the various amendments on the structural aggregate stability of the soils. At the end of the first cropping season, the index identified the soil amended with BA_{50} +NPK $_{150}$ (61%) as the most stable contrary to that by percent aggregate stability index, which had BA_{10} + PM_{20} as the most stable. The least was NPK₇₅ (44%), which was however statistically (p<0.05) the same with BA_{50} . Soils amended with PM_5 , NPK $_{150}$, BA_{50} +PM₁₀, BA_{10} +PM₂₀ and BA_{100} +NPK $_{75}$ did not alter the aggregate stability significantly as indicated by the percentage state of aggregation index. Percent state of aggregation increased remarkably at the end of the second cropping season. It ranged from 46% in BA_{100} +PM₂₀ that differed significantly from the control.

The mean weight diameter (MWD), aggregate stability index ranged from 0.42 in $BA_{10}+PM_{20}$ to 0.6 in $BA_{50}+NPK_{150}$ while the control was 0.50 at the end of the first cropping season. Sole doses of mineral fertilizer (NPK 20: 10: 10), low rate of boiler ash (10tha⁻¹) and a blend of $BA_{10} + PM_{20}$ induced disaggregation of the soil. The $BA_{50}+NPK_{150}$ had the highest value at both seasons. At the end of the second cropping season, stability increased in all

 Table 13: Effect of different rates and combinations of boiler ash, poultry droppings and

 NPK 20:10:10 on soil aggregate stability as evaluated using different aggregation

 indices

	A.S (%)	%	5 S.A	Ν	ÍWD
Treatment	1 st C.S	2 nd C.S	1 st C.S	2 nd C.S	1 st C.S	2 nd C.S
BA ₁₀₀	64.1	51.2	56.6	59.5	0.561	0.438
BA ₅₀	53.6	54.0	44.9	56.5	0.561	0.457
BA_{10}	57.1	56.6	51.0	69.1	0.483	0.499
PM_{20}	61.3	57.3	52.0	71.0	0.549	0.682
PM_{10}	59.3	57.2	51.1	69.2	0.574	0.649
PM ₅	56.0	57.2	48.1	66.9	0.515	0.553
NPK ₃₀₀	53.6	70.1	46.2	75.2	0.456	0.688
NPK ₁₅₀	54.2	60.7	47.6	72.6	0.458	0.600
NPK ₇₅	51.9	56.7	44.2	68.9	0.642	0.561
$BA_{100} + PM_5$	59.9	46.3	51.4	59.4	0.545	0.668
$BA_{50} + PM_{10}$	57.6	61.7	49.6	72.2	0.570	0.638
$BA_{10} + PM_{20}$	66.5	67.0	50.3	74.6	0.416	0.658
$BA_{100}\ +\ NPK_{75}$	56.9	54.2	48.7	61.9	0.558	0.566
$BA_{50} + NPK_{150}$	64.2	62.6	60.7	71.3	0.693	0.755
$BA_{10} + NPK_{300}$	58.4	61.6	51.2	70.4	0.495	0.599
No amendment	56.0	57.8	48.9	63.8	0.502	0.433
F-LSD _{0.05}	5.335	6.157	1.701	3.784	0.0065	0.0381

1st C.S= First cropping season, 2nd C.S= Second cropping season, A.S =aggregate stability

%S.A =percent state of aggregation, MWD=mean weight diameter, F-LSD_{0.05}= Fishers least significant difference at 5% level of probability.

treatments except in BA_{100} and BA_{50} . High doses of boiler ash were only effective as an aggregating agent at the first cropping season. The MWD aggregation index identified the superiority of BA_{50} +NPK $_{150}$ treatment over others. According to the MWD data, aggregate stability generally increased at the end of the second cropping season over that of the first cropping season.

Aggregate stability is a complex parameter, which results from interaction of many variables whose net effect may be dispersion or stability. The mean weight diameter of waterstable aggregates (MWD) is a very useful index for assessing the macro aggregate stability status of soils to water forces. Higher values indicate better stability. The findings in this study agree with that of Mbagwu (1994) who obtained a positive correlation between silt fraction and the mean weight diameter. The BA_{50} +NPK ₁₅₀ treated plots with the highest MWD value (0.76) also had the highest silt content at the end of the second cropping season. It was also in agreement with Gross et al. (2006) who noted that boiler ash affects aggregate size distribution and cause loss of soil structure. It causes slaking of macro-aggregates (1000-4000 m) which are highly correlated with decrease of MWD. The high sodium content (610mgkg) of the ash (Table 6) used in this study, may have resulted in breaking up of the soil aggregates and in increasing colloidal mobility. Since, it has been confirmed that strong electric repulsive force (*1000 atm) resulting from particle surface plays an important role in soil colloid interactions. High concentration of K+ could limit clay dispersion and maintain macro aggregate stability, while Na+ could accelerate aggregate breakdown (Levy and Torrento, 1995; Li et al.2009, Li et al. 2013, Aziz, and Karim, 2016). The oxides of Al, Fe, Mg and Mn are the important chemical constituents, which enhance aggregate stability. The negligible level of Al in the boiler ash treated plots may have contributed to its lower aggregate stability. Structural stability of soils was related to the type and content of organic matter added to the soil. Materials with high nitrogen content breakdown in soil much readily when moisture and temperature are adequate because they have high sugar and low lignin contents (Valis and Jones, 1973). This rapid breakdown of organic matter is not conducive to the formation of stable aggregates. This may have been responsible for lower stability in the poultry droppings treated soils at the end of the second cropping season when compared with the mineral fertilizer. The high stability of the mineral fertilizer treated plots at the second cropping season may have resulted from improved faunal and microbial activities arising from the high nutrient content of the fertilizer.

The results also revealed the differences exhibited by different aggregate stability indices in assessing the structural stability of ash-amended soils

4.4.7. Electrical Conductivity

Table 14 showed that soil electrical conductivity (EC) measured at the end of the first cropping season was not significantly affected by the application of the amendments. However, at the end of the second cropping season, some of the amendments significantly (p<0.01) reduced the soil electrical conductivity relative to the non -amended soil (Table14). The EC values ranged from 6.5dsm⁻¹ in PM₁₀ to 10.5 dsm⁻¹ in BA₁₀₀ + PM₅ while, the control was 9.5 dsm⁻¹. Application of low levels of boiler ash (BA₁₀) and poultry droppings decreased EC significantly (p<0.01) relative to the control. The BA₁₀₀ + PM₅, which had the maximum level of EC (10.5dsm⁻¹), however, it did not differ significantly from the control (9.5dsm⁻¹).

The result corroborates that of Jamil and Qasim (2008) who observed non-significant effect of different rates of boiler ash from sugarcane bagasse on soil EC and organic carbon status of the soil. In contrast, Kumar (2002) observed that coal fly ash application particularly in higher amount increased the pH and EC of the soils. Tsadilas (2014) also noted that soil pH and EC may be affected by fly ash in both directions i.e. decrease or increase depending on the fly ash characteristics and degree of weathering (ageing) and sulphur content.

	Electrical Conduction	vity (dsm- ¹)
Treatment	I st C.S	2 nd C.S
BA ₁₀₀	16.5	8.1
BA ₅₀	18.5	9.5
BA ₁₀	20.5	7.5
PM ₂₀	18.0	7.0
PM_{10}	17.5	6.5
PM ₅	18.5	7.0
NPK ₃₀₀	20.5	8.0
NPK ₁₅₀	19.5	7.5
NPK ₇₅	16.5	8.0
$BA_{100} + PM_5$	18.0	10.5
$BA_{50} + PM_{10}$	20.0	8.5
$BA_{10} + PM_{20}$	19.0	7.5
$BA_{100} + NPK_{75}$	20.5	8.5
$BA_{50} + NPK_{150}$	19.5	7.5
$BA_{10} + NPK_{300}$	20.5	7.5
No amendment	20.5	9.5
F-LSD(0.05)	n.s	1.40

 Table 14: Impact of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on soil electrical conductivity.

1st C.S= First cropping season, 2nd C.S= Second cropping season, n.s= non-significant at 5% level, $F-LSD_{0.05}$ = Fishers least significant difference at 5% level of probability.

4.5. Treatment Effects on Soil Chemical Properties

4.5.1. Soil pH

The amendments exerted significant (p<0.01) influence on the soil pH at both cropping seasons (Table 15). Application of boiler ash at the rate of 10tha⁻¹ (BA₁₀) increased pH from 5.2 in the control plot to 6.5 while 100tha⁻¹ (BA₁₀₀) rate increased it to 7.6. All the plots amended with different rates of sole NPK mineral fertilizer and poultry droppings at the rate of 5tha⁻¹ did not significantly influence the soil pH. Combined application of BA with either PM or NPK 20:10:10 increased the soil pH relative to the control (Table 15). The highest pH value (7.7) was obtained in plots amended with a combination of 10tha⁻¹ BA and 20tha⁻¹PM (BA₁₀ + PM₂₀); and 50tha⁻¹BA and 150kgha⁻¹NPK (BA₅₀ + NPK ₁₅₀). In combinations involving BA and NPK, the pH increased as the level of boiler ash increase. This therefore, indicates that addition of BA obliterated the acidic effect of the N.P.K 20:10:10 fertilizer by raising the pH. The pH in KC1 followed the same trend.

The increase in pH due to the application of BA may be attributed to ash accretion as ash residues are generally dominated by carbonates of alkali and alkaline earth metals, variable amounts of silica, heavy metals, phosphates and small amounts of organic and inorganic N (Raison. 1979.). The CaO of the boiler ash might have reacted with H_2O to produce OH⁻ and other ionic forms in the soil solution.

$$CaO + H_2O$$
 $Ca (OH)_2$ $Ca^{2+} + OH$

The mechanism suggested by Ano and Ubochi (2007) was microbial decarboxylation of Caorgano complex leading to the release and consequent hydrolysis of Ca ions. The hydroxyl ion released reacts with the exchangeable $H^+ + Al^{3+}$ to form water insoluble Al (OH₃) respectively. This may have explained the non-detectable Al^{3+} in the boiler ash based treatments (Table 16). These reactions and the presence of Na may have explained the high pH values. Another reason for the increase in soil pH due to the application of BA could be the high surface area and porous nature of BA that increases the cation exchange capacity (CEC) of the soil (Agusalim *et al.*, 2010). Thus, there could be a chance for Al and Fe to bind with the exchange site of the soil. Agusalim et al. (2010) and Nigussie et al. (2012) have reported the decrease in exchangeable Al as found in this study.

Similarly, the poultry droppings increased the pH; however, it did not differ significantly in response to changes in application rate. This may be attributed to the

	pH (H ₂ 0)		pH (KCL)	
Treatment	I st C.S	2^{nd} C.S	I st C.S	2^{nd} C.S
BA_{100}	7.6	7.4	6.8	6.9
BA ₅₀	7.7	7.4	7.0	6.8
BA_{10}	6.5	6.4	5.7	6.3
PM ₂₀	6.7	6.6	5.4	5.5
PM_{10}	6.1	6.6	5.1	4.8
PM ₅	5.6	5.8	4.2	4.2
NPK ₃₀₀	5.3	5.9	4.1	4.1
NPK ₁₅₀	5.2	7.1	4.1	6.8
NPK ₇₅	5.5	5.1	4.2	4.1
$BA_{100} + PM_5$	7.3	7.3	7.0	6.9
$BA_{50} + PM_{10}$	6.8	7.0	6.3	6.6
$BA_{10} + PM_{20}$	7.7	6.6	7.2	5.6
$BA_{100}\ +\ NPK_{75}$	7.5	7.4	6.6	7.0
$BA_{50} + NPK_{150}$	7.4	7.2	7.0	6.5
$BA_{10} + NPK_{300}$	6.4	6.0	5.1	5.1
No amendment	5.2	5.3	4.1	4.0
F-LSD _(0.05)	0.43	0.37	0.57	0.26

 Table 15: Impact of different rates of boiler ash, poultry droppings NPK 20:10:10 and their

 Combinations on soil pH

1st C.S= First cropping season, 2nd C.S= Second cropping season, n.s= non-significant at 5% level, F-LSD_{0.05}= Fishers least significant difference at 5% level of probability.

buffering reactions in the experimental soil, which was characteristic of the high organic matter content of the manure (Tsadilas *et al.* 2002). The non-significant difference between the control and NPK ₃₀₀ plots agrees with the findings of Ayeni and Adeleye (2009).

The result of increased pH in BA treated soil is indicative of the fact that BA is a potential agent for low soil pH remediation and soil fertility improvement. It should however be noted that the modification of soil pH could adversely affect soil-nutrient supply as well. Campbell (1990) suggested that the potential hazard to soil posed by changes in pH and salt concentrations are of a concern than trace metals. High pH leads to precipitation of micronutrients and high salinity increases osmotic pressure and hence affects plant water uptake. Higher pH also leads to solubilization of organic matter, which may lead to the removal of sinks of metals in the soil and mobilization of colloids. This enhances metal transport and has a negative impact on soil biota (Chirenje and Ma, 1999).

4.5.2. Organic Carbon and Total Nitrogen

The data on changes on percent organic carbon (Table16) revealed that the amendments did not significantly influence the organic carbon content of the soil at the end of the first cropping season. However, at the end of the second cropping season, soil organic carbon differed significantly (p<0.01) and ranged from 0.79 in PM₅ to 1.49 mg kg⁻¹ in the BA₁₀₀ + NPK $_{75}$ amended plots, while the control was 0.97 mg kg⁻¹. The highest value was obtained under the residual effects of integrated fertilization sources including BA and NPK as compared to sole application of BA, PM or NPK.

The non- significant effect at the first cropping season collaborates the findings of Haynes (2005) and Liu *et al.* (2013) who observed that soil organic carbon is not sensitive to short term changes resulting from soil or crop management practices due to high background level and natural soil variability. At the end of the second cropping season, organic carbon showed a more elastic response to increasing rates of BA amendments than the poultry dropping,. Consequently, rates above PM_{10} (10 tha⁻¹) did not make significant contribution to the organic carbon. This finding agrees with that of Das *et al.* (2013) who observed that SOC tended to increase significantly when fly ash from paper mill was integrated with recommended dose of fertilizer (RDF) and farmyard manure. The significant difference observed only at the second cropping season indicates that organic materials in the wastes continuously decomposed during the period, added organic matter to the soil, and has

	% Organic carbon(mg kg ⁻¹)		Total nitrogen (m	ng kg ⁻¹)
Treatment	1 st C.S	2 nd C.S	1 st C.S	2 nd C.S
BA ₁₀₀	0.81	1.23	0.119	0.114
BA ₅₀	0.74	0.97	0.129	0.100
BA_{10}	0.60	0.86	0.096	0.051
PM ₂₀	0.73	1.10	0.095	0.086
PM_{10}	0.81	1.10	0.082	0.090
PM_5	0.73	0.79	0.080	0.074
NPK300	0.71	0.90	0.084	0.059
NPK ₁₅₀	0.79	1.10	0.078	0.089
NPK ₇₅	0.72	0.83	0.055	0.060
$BA_{100} + PM_5$	0.93	1.42	0.155	0.144
$BA_{50} + PM_{10}$	0.76	0.97	0.100	0.103
$BA_{10} + PM_{20}$	0.65	0.90	0.088	0.088
$BA_{100}\ +\ NPK_{75}$	0.99	1.49	0.113	0.124
$BA_{50} + NPK_{150}$	0.78	1.09	0.111	0.095
$BA_{10} + NPK_{300}$	0.65	0.86	0.094	0.080
No amendment	0.60	0.97	0.081	0.082
F-LSD(0.05)	n.s	0.10	0.029	0.0108

 Table 16: Impact of different rates of boiler ash, poultry droppings, N.P.K 20:10:10 and

 their combinations on soil organic matter and nitrogen composition

1st C.S= First cropping season, 2nd C.S= Second cropping season, n.s = non-significant at 5% level, $F-LSD_{0.05}$ = Fisherøs least significant difference at 5% level of probability.

better residual effect. The low carbon content under NPK fertilizer was mostly attributed to rapid mineralization of organo-mineral complex (Yoshida and Padre, 1975). These findings are in tandem with that of Yeledhelli *et al.* (2007) and Buddhe *et al.* (2014).

The total soil nitrogen increased with increasing quantity of the amendments in form of BA at both seasons. Mean total nitrogen in the treatment receiving no amendment at both seasons was 0.08 mg kg⁻¹ (Table16). Highest total soil nitrogen (0.155 and 0.144 mg kg⁻¹) were obtained in plots amended with BA_{100} + PM₅ at first and second cropping seasons respectively. Relative to the control treatment, soil total nitrogen in plots amended with BA_{50} , PM_{20} , NPK₃₀₀, and BA_{100} +PM₅ increased by 59%, 17%, 4%, and 91% respectively. Total soil nitrogen increased linearly with boiler ash addition in both years. Sole application of high levels of BA (BA_{100}) significantly increased soil N by 47% and 39% at the first and second cropping seasons respectively. While, sole PM and NPK treatments had slight non-significant increases. Furthermore, addition of lower levels of BA to high levels of PM or NPK did not result in a significant increase in the soil total nitrogen. However, combined application of higher doses of BA with lower dose of PM or NPK increased total N significantly (P<0.01) relative to the control.

The reduction in total N experienced in the PM and NPK treated plots may be ascribed to their low C: N ratio and rapid rate of mineralization, which might have resulted to the loss of NH₃ over time. Higher crop uptake of the nutrients in the PM or NPK treated soils may also have contributed to the depletion. The observation of significant effects on soil N at the end of the second cropping season indicate that the materials were still decomposing and nutrients mineralized up to two years after application. The findings collaborates that of Kahl *et al.* (1996), Yeledhelli *et al.*, (2002); Saarsalmi *et al.* (2010), Abdulraheem *et al.* (2012), Akinmutimi, (2014). They opined that although, BA is low in nitrogen, its application to soil significantly (p<0.01) affected nitrogen mineralization process probably by altering the activity and changing the composition of soil microbes through changes in soil chemical properties. The higher status of total N under treatments involving higher doses of BA can be ascribed to fixation and accumulation of organic N (Savant and De Datta, 1982).

4.5.3. Available Phosphorus (P)

Data on Table 17, indicate that the highest soil available P (124.61 mgkg^{-1}) was recorded in the plots amended with BA₅₀ + NPK ₁₅₀ and BA₁₀₀ + PM₅ (117.52 mgkg^{-1}) at the end of the first and second cropping seasons, respectively, while, values from the control

	Total phospho	orus	Sulphur	
	ííííí	í mgkg ⁻¹ í	ííííí	ííí.
Treatment	1 st C.S	2^{nd} C.S	1 st C.S	2^{nd} C.S
BA ₁₀₀	117.39	91.28	0.115	0.157
BA ₅₀	110.67	77.91	0.115	0.178
BA_{10}	67.40	57.16	0.115	0.188
PM_{20}	42.61	34.86	0.130	0.173
PM_{10}	32.99	26.30	0.118	0.196
PM ₅	21.99	24.93	0.139	0.283
NPK300	9.05	19.09	0.141	0.126
NPK ₁₅₀	18.81	15.84	0.120	0.138
NPK ₇₅	13.17	13.65	0.136	0.148
$BA_{100} + PM_5 \\$	109.30	117.52	0.131	0.179
$BA_{50} + PM^{10}$	98.68	85.94	0.135	0.187
$BA_{10}+PM_{20}$	85.86	84.50	0.147	0.391
$BA_{100} + NPK75$	122.47	73.53	0.112	0.189
$BA_{50} + NPK_{150}$	124.61	105.90	0.130	0.137
$BA_{10} + NPK_{300}$	58.67	45.79	0.132	0.181
No amendment	16.34	16.23	0.138	0.198
F-LSD(0.05)	7.738	4.663	0.0123	0.0046

Table 17: Impact of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on soil phosphorus and sulphur contents

1st C.S= First cropping season, 2nd C.S= Second cropping season, F-LSD_{0.05}= Fishers least significant difference at 5% level of probability

plots were 16.34 and 16.23 mgkg⁻¹ at the end of the first and second cropping seasons respectively. The application of BA at the rate of 10, 50 and 100 tha⁻¹ increased available P content of the amended soil significantly (P< 0.01) at the end of both cropping seasons. Application of BA at the rate 10tha⁻¹ (BA₁₀) increased available P (67.4 mgkg⁻¹) higher than the highest rates of either PM₂₀ (42.6 mgkg⁻¹) or NPK₃₀₀ (9.1 mgkg⁻¹).

The available P content of the soil increased with increase in the quantity of BA added probably due to the high content of P in the ash (Table 6). Available P increase can as well be attributed to traces of P probably released from Al^{3+} in line with the observation of Ikpe *et al.* (1997). The higher ash application rates increased the soil pH, which likely increased the solubility and availability of P in the soil solution. Since phosphate availability/absorption is highest at the 6-7 pH range, the phosphate availability likely increased at BA₅₀ and BA₁₀₀ (pH 7.5) relative to lower ash level. The favorable effect of BA on P availability may also be ascribed to its effect on biotic activity. The slow nutrient release properties of the ash may have accounted for the higher P content of the soil at the end of the second than the first cropping season.

Matte and Kene (1995), Mahato *et al.* (2005) and Das *et al.* (2013) have reported similar increases in available P content. However, the finding is contrary to that of Patterson (2001) and Ram *et al.* (2006) who noted that only a small portion of applied P in ash is in available form and as such should be highlighted as a draw back in the application of ash to soils.

4.5.4 . Concentration of Sulphur

Application of BA significantly (p < 0.01) reduced the sulphur content of the postharvest soil at the end of the first cropping season (Table17) relative to the control (0.138mgkg⁻¹). The reduction was independent of the rate of application. Similarly, poultry droppings and NPK 20:10:10 did not significantly influence the sulphur composition of the soil. Blending BA with either PM or NPK decreased the reduction, although not significantly.

The treatment $BA_{10} + PM_{20}$ had the highest sulphur content (0.147mgkg⁻¹) followed by NPK₃₀₀ (0.141mgkg⁻¹). A similar trend was observed at the end of the second cropping season.

4.5.5. Exchangeable Bases

The concentrations of soil exchangeable bases (Ca, Mg, K, Na) were significantly (P<0.01) influenced at both cropping seasons following soil amendment with the different fertilization sources (Table 18). At the end of the first cropping season, the highest Ca content (7.00 cmolkg¹)⁻ was observed in PM₂₀ treated plots, although it was at par with BA₁₀₀ amended plots. The lowest response (2.8) was observed in BA₅₀ treated plots, while the value from the control plots was 4.1cmol kg⁻¹ at both seasons. Integration of BA with either PM or NPK fertilizer did not lead to additional increase in the calcium status of the soil. At the end of the second cropping season, calcium concentration in all the treatments were significantly (p<0.01) lower than that of the control plot (4.1cmol kg⁻¹). The least value (1.30 cmol kg⁻¹) was observed in the NPK₇₅ treated plots.

The highest magnesium content of 17.8 cmolkg⁻¹ recorded in $BA_{100} + NPK_{75}$ at the end of the first cropping season was significantly (P<0.01) higher than all the other treatments except $BA_{100} + PM_5$. It was more pronounced in the BA treated soils. They increased with increasing level of BA amendment but not significantly above the 50 tha⁻¹ rate. A similar trend was observed at the end of the second cropping season.

The results also revealed that sole application of 10 and 100 tha⁻¹ BA significantly (p>001) increased soil sodium (Na) content relative to the control (0.71 Cmolkg⁻¹). All sole PM and NPK rates did not differ significantly with the control. However, blending them with BA significantly (p<0.01) enriched the soil with Na. The soil sodium content increased remarkably at the end of the second cropping season with the BA₁₀+PM₂₀ (0.391Cmolkg⁻¹) followed by PM₅ (0.283 Cmolkg⁻¹) as the highest, while the least was observed in NPK₃₀₀ (0.126 Cmolkg⁻¹).

Boiler ash amended plots were marked by the abundance of potassium (K) which persisted two years after application. At the end of the first cropping season, the K content of the control plot was 0.193 cmol kg⁻¹ while, BA_{100} treated plot was 0.461cmol kg-1 showing 138.8% increase. It was statistically the same with BA_{50} treated plots. The highest increase was observed when the BA_{100} was blended with PM_5 ($BA_{100} + PM_5$). Thus, $BA_{100}+PM_5$ rate was the optimum for mobilization of K followed by NPK₁₅₀. Poultry droppings treatments were less effective. Blending NPK₃₀₀ with BA_{10} raised the K value to 0.41cmol kg⁻¹. The K value generally reduced at the end of the second cropping however, there were significant differences (P<0.01) among treatments. BA application increased the K content of the soil from 0.95 cmol kg⁻¹ in the control plot to 0.235 cmol kg⁻¹ in the BA₁₀₀ treated plots which
	Ca ²⁺	Mg ²⁺		Na ⁺		K		
				cm	ol kg-1			-
Treatment	1 st C.S	2 nd C.S						
BA_{100}	6.65	3.15	11.50	7.5	0.88	0.157	0.461	0.235
BA ₅₀	2.80	2.25	9.55	9.8	0.80	0.178	0.454	0.220
BA_{10}	4.05	1.95	2.60	1.7	0.92	0.188	0.365	0.080
PM_{20}	7.00	2.70	7.20	1.5	0.79	0.173	0.237	0.115
\mathbf{PM}_{10}	5.55	2.30	0.80	1.7	0.75	0.196	0.257	0.110
PM ₅	4.55	1.50	1.05	1.5	0.77	0.283	0.294	0.120
NPK ₃₀₀	4.40	1.65	0.45	1.6	0.81	0.126	0.227	0.140
NPK150	5.45	1.45	1.70	1.2	0.71	0.138	0.535	0.110
NPK ₇₅	4.25	1.30	0.86	1.3	0.66	0.148	0.110	0.235
$BA_{100} + PM_5 \\$	4.05	2.65	15.90	10.5	0.77	0.179	0.394	0.075
$BA_{50} + PM_{10}$	6.35	2.35	4.35	5.4	0.90	0.187	0.383	0.210
$BA_{10}+PM_{20}$	4.10	2.55	4.25	2.5	0.86	0.391	0.411	0.200
$BA_{100} + NPK_{75}$	6.60	2.50	17.80	11.4	0.88	0.189	0.558	0.265
$BA_{50} + NPK_{150}$	5.45	2.05	11.95	7.1	0.87	0.137	0.475	0.250
$BA_{10} + NPK_{300}$	4.70	1.65	2.15	2.4	0.85	0.181	0.329	0.170
No amendment	4.10	4.10	0.85	1.0	0.71	0.198	0.193	0.095
F-LSD(0.05)	0.049	0.226	2.141	0.556	0.129	0.0046	0.084	0.024

Table 18: Impact of different rates of boiler ash, poultry droppings NPK 20:10:10 and their admixture on soil exchangeable cations

1st C.S= First cropping season, 2nd C.S= Second cropping season, F-LSD_{0.05}= Fishers least significant difference at 5% level of probability.

however was statistically (p<0.01) the same with BA_{50} . All PM and higher rates of NPK 20:10:10 had lower values relative to high rates of BA. Blending NPK₃₀₀ with BA_{10} reduced the value from 0.235 to 0.170 cmol kg⁻¹.

Table 18 indicates that BA alone or with PM or NPK fertilizer increased soil exchangeable bases (Mg, K, Na) except Ca compared to the control, PM alone or NPK alone. The parameters increased increase in BA.The observed substantial enrichment of the soil with exchangeable bases (Ca, Mg, K, Na) following BA application were in tandem with that of several researchers (Naylor and Schmidth, 1989; Vest *et al.*, 1999; Rautaray *et al.*, 2003; Haraldsen et al. (2012, Adeji-Nsiah and Obeng, 2013; Buddhe, 2014). Kahl *et al.* (1996) also observed minimal effects at low ash dose rate, but heavier additions overload the soils buffer capacity. From this study, one can infer that the assertion by Naylor and Schmidt (1986) that availability of K in BA was a linear function of the amount added to the soil was limited to doses not exceeding 50tha⁻¹. This may have accounted for why Paterson (2001) observed minimal differences in soil available nutrient levels between 12.5 and 25tha⁻¹ ash application rate.

The reported increase in the soil content of K, Ca, Mg, due to application of combined BA and PM or NPK fertilizer were similarly observed byYeledhelli *et al.* (2007), Adejobi *et al.* (2011), Abdulraheem *et al.* (2012) and Akinmutimi (2014). In addition, oil palm bunch ash and their combined use with NPK fertilizer at reduced level have been reported to increase soil OM, N, P, K, Ca, and Mg (Ojeniyi, 2010). The superiority of BA amended soils in increasing the soil exchangeable bases may be attributed to the inherent composition of the BA (Table 6) and its influence on increased soil pH,

4.5.6. Cation Exchange Capacity (CEC) and Percent Base Saturation.

Results of the effects of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on cation exchange capacity and percent base saturation are given in Table 19. The CEC was significantly (p< 0.01) increased by application of BA at the end of the first cropping season. The highest CEC value (26.5 cmol Kg⁻¹soil) was obtained from plots treated with (BA₁₀₀ + NPK₇₅) (Table 19). It was followed by BA₁₀₀ + PM₅ while the least (9.0 cmol Kg⁻¹ soil) was obtained from BA₁₀ + NPK₃₀₀, which, however, did not differ significantly from the control. BA application did not significantly influence the soil CEC at the end of the second cropping season. Significant reduction in CEC was observed in PM and NPK treated plots but blending them with different rates of BA obliterated the reduction. The inherent

	Cation exch (cmol kg	Cation exchange capacity (cmol kg ⁻¹)		base saturation (%)
Treatment	1 st C.S	$2^{nd}C.S$	1 st C.S	2^{nd} C.S
BA_{100}	19.58	18.55	99.5	76.1
BA_{50}	14.39	19.20	94.6	51.2
BA_{10}	11.60	19.40	78.2	23.8
PM ₂₀	15.30	16.00	95.4	24.3
PM_{10}	10.60	15.60	69.8	26.4
PM ₅	11.50	15.60	61.5	24.2
NPK ₃₀₀	11.40	16.80	51.3	20.9
NPK150	11.10	14.60	72.3	24.2
NPK ₇₅	11.25	19.20	60.4	21.7
$BA_{100} + PM_5$	22.60	19.20	92.8	48.4
$BA_{50} + PM_{10}$	12.15	19.40	97.8	33.3
$BA_{10} + PM_{20}$	10.45	19.40	93.7	33.3
$BA_{100} + NPK_{75}$	26.50	19.80	98.0	55.9
$BA_{50} + NPK_{150}$	18.95	19.90	95.6	42.8
$BA_{10} + NPK_{300}$	9.00	19.80	90.8	23.6
No amendment	10.65	19.40	54.3	26.8
F-LSD(0.05)	1.905	1.99	8.986	28.86

 Table 19: Impact of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on soil cation exchange capacity and percent base saturation

1st C.S= First cropping season, 2nd C.S= Second cropping season, F-LSD_{0.05}= Fishers least significant difference at 5% level of probability.

characteristics of the BA may have been responsible for the higher CEC. Available evidence also suggested that on a mass basis, the intrinsic CEC of BA is consistently higher than that of whole soil, clays or soil organic matter (Kohli et *al.* 2009).

Percent base saturation was significantly (p<0.01) improved by increasing levels of the BA amendments after the first cropping season. Variation between BA_{50} and BA_{100} rates were not significant at both seasons. Among the PM treated plots, only PM_{10} differed significantly (p<0.01) from the control in first cropping season. However, blending the different rates of PM or NPK with BA increased the percent base saturation significantly (p<0.01) relative to the control.

The increases in CEC and percent base saturation were mainly attributed to the inherent properties of the BA itself as evidenced from the characteristic properties (Table 6). The results are similar to those reported by Miller (1999) and Yeledhelli *et al.;* (2007). In this study, the increase in CEC and a decrease in the exchangeable acidity because of BA application means that, not only that the relative proportion of cation exchange sites occupied by base cations increased but also the concentration of base cations.

4.5.7. Content of Mobile Aluminum and Hydrolytic Acidity

The mobile aluminum content of the control plots was 1.5 mg Kg⁻¹ (Table 20). Application of BA at all levels significantly (p<0.01) diminished the mobile aluminum content to non-detectable level at both seasons. High rates of BA were also able to depress it when combined with low level of poultry droppings.

At the second cropping season, all sole and combinations of BA were below detection level. This could be attributed to the increase in CEC imparted on the soil by BA amendments. Agusalimi et al. (2010) and Nigussie et al. (2012) have reported similar results.

Hydrolytic acidity of the control plot at the first cropping season was 1.5 cmolKg⁻¹ soils (Table 20). Application of BA increased the hydrolytic acidity to 2.7 cmolKg⁻¹ soil, which however did not differ in respect to the rate of application. The lowest value of hydrolytic acidity (1.10 cmolKg⁻¹ soil) was obtained after applying the BA₁₀ + PM₂₀. Correspondingly, as in the case of soil reaction changes, the lowest drop in hydrolytic acidity was obtained after applying BA₁₀ +PM₂₀. In general, the combination was more effective in decreasing hydrolytic acidity. Application of low levels of NPK 20:10:10 increased the hydrolytic acidity of the soil

significantly (p<0.05) at the end of the second cropping season. All other treatments diminished the acidity significantly.

4.5.8 . Exchangeable Sodium and Sodium Adsorption ratio.

Table 21 shows that the exchangeable sodium percentage (ESP) and sodium adsorption ratio (SAR) of the soil were significantly (p<0.05) influenced by the application of boiler ash, poultry droppings, NPK 20:10:10 and their combinations after the first and second cropping seasons. After the first cropping season, exchangeable sodium percentage ranged from 3.32 in $BA_{100} + NPK_{75}$ to 9.44% in $BA_{10}+NPK_{300}$. The low rates of boiler ash either sole or combined with poultry droppings or NPK 20:10:10 increased the ESP, while high rate reduced it. The result agrees with that of Tiwari *et al.* (1992). The ESP dropped dramatically from the first to the second cropping season. At the second cropping season, it ranged from 0.67% in the control plot to 1.15% in the PM₁₀ treated plot.

Similar trend was also observed with the SAR, which was generally low. The finding agrees with Birtschi (2000) who found non-significant influence of ash application on SAR. The findings indicates that although, boiler ash is a source of both electrolytes and alkalinity (Reichert and Norton, 1994), the presence of sodium in exchangeable form was low and the potential hazard from the exchangeable sodium levels in the amended soil was also low.

	Exchange	Exchangeable Al ³⁺		eable H ⁺	
	(mg K	(g ⁻¹)	(cmoll	Kg ⁻¹)	
Treatment	1 st C.S	2^{nd} C.S	1 st C.S	2^{nd} C.S	
BA_{100}	0.00	0.00	2.7	1.9	
BA_{50}	0.00	0.00	2.3	1.5	
BA_{10}	0.00	0.00	2.4	1.5	
PM_{20}	0.20	0.00	1.9	1.3	
PM_{10}	0.35	0.3	2.5	1.3	
PM_5	0.65	0.7	2.5	1.7	
NPK300	1.65	1.3	1.7	2.7	
NPK ₁₅₀	1.25	1.3	2.1	3.7	
NPK ₇₅	1.15	0.7	2.2	1.3	
$BA_{100} + PM_5$	0.00	0.0	2.5	1.9	
$BA_{50} + PM^{10}$	0.00	0.0	1.7	1.7	
$BA_{10} + PM_{20}$	2.5	0.0	1.1	1.3	
$BA_{100} + NPK_{75}$	2.5	0.0	1.9	1.9	
$BA_{50} + NPK_{150}$	2.0	0.0	2.2	1.7	
$BA_{10} + NPK_{300}$	0.5	0.0	2.1	1.7	
No amendment	1.5	0.0	1.5	2.5	
F-LSD(0.05)	0.153	0.564	0.345	0.206	

 Table 20: Impact of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on soil mobile aluminum and hydrolytic acidity

 1^{st} C.S= First cropping season, 2nd C.S= Second cropping season, F-LSD_{0.05}= Fishers least significant difference at 5% level of probability.

	Exchangeable	Sodium Percentage	Sodium Ad	sorption Ratio
	(%	6)		
Treatment	1 st C.S	2 nd C.S	1 st C.S	2 nd C.S
BA ₁₀₀	4.49	0.97	0.204	0.055
BA ₅₀	5.56	0.89	0.228	0.049
BA ₁₀	7.93	0.88	0.357	0.089
PM ₂₀	5.16	0.75	0.210	0.059
PM ₁₀	7.08	1.15	0.298	0.090
PM ₅	6.70	0.83	0.325	0.075
NPK ₃₀₀	7.11	1.01	0.368	0.094
NPK ₁₅₀	6.40	0.68	0.266	0.061
NPK ₇₅	5.87	0.73	0.292	0.087
BA ₁₀₀ + PM ₅	3.41	0.73	0.172	0.039
BA ₅₀ +PM ₁₀	7.41	1.03	0.275	0.072
BA ₁₀ + PM ₂₀	8.23	1.08	0.298	0.093
BA ₁₀₀ + NPK ₇₅	3.32	0.91	0.182	0.048
BA ₅₀ + NPK ₁₅₀	4.59	0.90	0.209	0.060
BA ₁₀ + NPK ₃₀₀	9.44	0.81	0.325	0.080
No amendment	6.67	0.67	0.319	0.058
F-LSD(0.05)	1.720	0.145	0.0625	0.0180

 Table 21: Effect of boiler ash, poultry droppings, NPK 20:10:10 and their combinations

 on Exchangeable Sodium Percentage and Sodium Adsorption Ratio

1st C.S= First cropping season, 2nd C.S= Second cropping season, F-LSD_{0.05}= Fishers least significant difference at 5% level of probability.

4.6 . Content of Boron, Cadmium, Manganese, Zinc and Copper in Soil.

Average boron (B) content in soil was significantly (p<0.01) influenced by the application of these amendments (Table 22). High levels of NPK 20:10:10 induced the highest (4.56 mgkg⁻¹) increase in soil boron at the end of the first cropping season. The control was 2.37mgkg⁻¹ soil. However, amending them with low levels of BA obliterated the increase and further reduced them to as low as 1.18mg kg⁻¹ B relative to the control. The differences obtained, however, did not exceed toxic limits. Neither fertilization of soil with BA, PM, NPK nor their combinations caused any significant change in the content of boron at the second cropping season .Significantly high levels of B in BA which can be detrimental to crop production were of no concern in this study and this may be due to the source, quality and age of BA used.

The accumulation of cadmium (Cd) increased with increasing rate of BA amendment to the peak of the agronomic rate of 50 tha⁻¹ and thereafter declines. Similar trend was observed at the end of the second cropping season. Result of this study indicated that one should be very careful in using BA considering the accumulation of Cd at the agronomic rate (50 tha⁻¹). Relative to sole BA application, combined application of BA with PM (p<0.01) reduced the soil Cd loading.

At the end of the first cropping season, high levels of BA increased Mn content of the soil. The total manganese content in the control soil sample was 6.75mg Kg⁻¹. Lower level of BA (BA₁₀) and all sole PM and NPK fertilizer had significantly (p<0.01) lower Mn content relative to the control. Similar trend was observed when the BA was combined with either PM or NPK. This result indicates that the high rates of BA were responsible for the Mn soil enrichment. The same trend was observed at the second cropping season.

Maximum zinc (13.5mgkg⁻¹) and copper (1.5mgkg⁻¹) were found in BA₁₀₀ and NPK ₃₀₀ treated soils respectively at the first yearøs post-harvest soil analysis. Boiler ash enriched the soil with Zinc linearly with increase in application rate. The control (2.10 mg kg⁻¹) was higher than all the NPK treated plots although not significantly different. All BA combinations with either PM or NPK significantly enriched the soil with zinc relative to the control. Similar result was obtained at the second cropping season.

The treatments did not significantly increase the soil Cu content at the first cropping season. At the end of the second cropping season, BA significantly (p<0.01) enriched the soil with Cu at the BA₁₀₀ and BA₁₀ rates. Blending the BA₅₀ rate with either PM₁₀ or NPK₁₅₀ increased the soil Cu availability from 0.04 to 1.14 and 1.63mg kg⁻¹ soil respectively.

	В		Cd		Mn		Zn		Cu	
$mgkg^{-1}$										
Treatment	1 st C.S	2 nd CS	1 st C.S	2 nd C.S						
BA ₁₀₀	3.45	4	0.295	0.637	11.55	12.04	13.5	14.5	1.21	1.84
BA_{50}	1.21	7	0.324	0.846	9.60	10.14	11.0	9.4	1.41	0.04
BA_{10}	2.35	2	0.309	0.595	3.05	3.37	4.0	6.5	1.08	1.48
PM ₂₀	1.19	9	0.295	0.596	3.50	3.85	4.0	4.3	1.01	1.05
PM ₁₀	1.19	5	0.320	0.503	5.35	6.46	2.9	11.7	0.97	1.04
PM ₅	1.19	7	0.124	0.616	1.85	2.04	1.8	11.3	0.79	2.43
NPK ₃₀₀	4.56	5	0.281	0.381	3.20	3.57	1.9	10.5	1.59	2.07
NPK ₁₅₀	4.56	10	0.283	0.415	5.85	6.31	1.7	14.7	1.35	1.54
NPK ₇₅	3.45	7	0.267	0.476	3.30	3.48	1.95	5.1	1.07	3.00
$BA_{100} + PM_5 \\$	3.44	11	0.255	0.549	10.35	10.81	13.3	5.9	1.18	1.66
$BA_{50} + PM_{10}$	1.18	11	0.259	0.565	7.15	7.77	9.2	6.7	0.83	1.14
$BA_{10}+PM_{20} \\$	1.18	11	0.263	0.475	4.90	5.62	4.85	7.1	1.47	2.39
$BA_{100}\ +\ NPK_{75}$	1.18	12	0.295	0.681	9.40	9.71	10.85	9.7	1.02	1.46
$BA_{50} + NPK_{150}$	1.19	5	0.279	0.584	10.75	11.33	11.85	5.4	1.37	2.26
$BA_{10} + NPK_{300}$	2.37	10	0.230	0.775	2.50	2.92	2.60	5.5	1.10	1.63
No amendment	2.37	7	0.226	0.373	6.75	7.09	2.10	12.7	1.71	1.04
F-LSD(0.05)	0.218	n.s	0.008	0.0142	0.610	0.269	1.225	0.418	n.s	0.059

Table 22: Impact of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on soil heavy metal content

1st C.S= First cropping season. 2nd C.S= Second cropping season, n.s= non-significant at 5% level,

F-LSD_{0.05}= Fishers least significant difference at 5% level of probability

Generally, the observed increase in soil micronutrients (Mn, Cu, Zn and Cd) in the BA amended plots may be attributed to the inherent properties of the boiler ash as evidenced from the characteristic properties (Table 6). Several researchers reported similar elevation of the concentration of micronutrients (Mn, Cu, Zn and Cd) in the soil after ash application (Naylor and Schmidth, 1989; Rautarary *et al.*, 2003; Buddhe *et al.*, 2014).

4.7.0. Treatment Effects on Crop Performance

4.7.1 Maize germination.

Application of the different treatments exerted significant (p<0.01) influence on percentage germination of maize grain (Table 23) at both cropping seasons. Minimum germination percentage (21.9%) was recorded in BA₁₀₀ (100tha⁻¹ BA) whereas it was maximum (83.3%) in PM₅ (5tha⁻¹ PM) treatment. The residual effects of the amendments on percentage grain germination indicate that the highest value (88.5%) was recorded in BA₁₀₀ + NPK₇₅, followed by BA₁₀₀ + PM₅ (84.4%) which was statistically the same with BA₁₀₀ and PM₁₀. The minimum germination was obtained in the plot treated with NPK₇₅, although not significantly different from the control. The germination percentage of grains in the BA treated plots increased with increase in the application rate.

The relative grain germination result (Table 23) indicates that it was only PM_5 treatments that increased grain germination although not significantly. It was observed that the higher the level of BA and PM, the higher the reduction in the relative grain germination. Blending the BA with either PM or NPK could not ameliorate the reduction.

The present findings of inhibition of germination by high levels of BA at the first year of application confirmed the earlier findings of Pawar and Dubey (1988); Wong and Wong (1989); Singh *et al.* (1992) and Swain and Padhi (2012). The results were, however, contrary to that of Singh *et al.* (1997) in Vicia faba plants; and Tripathy and Sahu (1997) in wheat grains, Sharma *et al.* (2001) and Pankaj *et al.* (2013) in maize; Yunsa *et al.* (2009) in barley.

The inhibition of germination by high rates of BA at the first cropping season may be attributed to the increased impedance offered by the soil/ ash matrix to germinating maize grains (Kalra *et al.;* 1997). It may also be attributed to the combined effect of osmotic pressure and toxicity of salts (Al-Moaikal, 2006) or due to the effect of added chloride ions (Gill *et al.,* 2002) which is high in the boiler ash (Table 6). However, their increased

	Germination		Relative grain germination		
	%		(RGG)		
Treatment	1 st C.S	2 nd C.S	1 st C.S	2 nd C.S	
BA ₁₀₀	21.9	83.3	0.29	1.11	
BA ₅₀	43.8	79.2	0.58	1.06	
BA ₁₀	70.9	63.5	0.94	0.85	
PM ₂₀	55.2	72.9	0.74	0.97	
PM ₁₀	69.8	83.3	0.93	1.11	
PM ₅	83.3	71.9	1.11	0.96	
NPK ₃₀₀	71.9	66.7	0.96	0.89	
NPK ₁₅₀	72.9	79.2	0.97	1.06	
NPK ₇₅	69.8	65.6	0.93	0.87	
BA ₁₀₀ + PM ₅	31.3	85.4	0.43	1.14	
BA ₅₀ +PM ₁₀	54.2	79.2	0.72	0.97	
BA ₁₀ + PM ₂₀	75.0	83.3	1.00	1.11	
BA ₁₀₀ + NPK ₇₅	31.2	88.5	0.42	1.18	
BA ₅₀ + NPK ₁₅₀	59.4	70.8	0.79	0.94	
BA ₁₀ + NPK ₃₀₀	62.5	79.2	0.80	0.97	
No amendment	75.0	75.0	-	-	
F-LSD _(0.05)	17.09	12.20			

Table 23: Mean effect of different rate of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on germination % and relative grain germination of maize grain

1st C.S= First cropping season, 2nd C.S= Second cropping season, F-LSD_{0.05}= Fishers least significant difference at 5% level of probability, RGG = Relative grain germination

germination percentage at the second cropping season may be due to higher soil moisture content (Table 10) and probable leaching of excess salts in the un-weathered boiler ash.

4.7.2. Maize Height

Maize plant height was determined at 4, 6, 8 and 10 weeks after planting (WAP) to evaluate the impact of the amendments at different stages of growth. The crop responded positively to the addition of all treatments except BA_{100} at the first cropping season (Table 24). Generally, $BA_{10} + PM_{20}$ produced the tallest plants with an average height of 189.5cm per plant, although it did not differ significantly from $BA_{50} + PM_{10}$ and $BA_{10} + NPK_{300}$. Application of BA at 100tha⁻¹ (BA₁₀₀) produced maize plant height that were shorter by 40, 51, 35 and 29% at 4, 6, 8 and 10 WAP respectively relative to the control. Among the BA rates BA_{50} gave the highest value (134.7cm per plant). Poultry droppings and NPK fertilizer linearly increased the plant height with increase in application rate. Combination of BA with PM or NPK had a synergistic effect on plant height increased from 51.1cm to 139.3 and 174.8cm respectively

At the second cropping season, all treatments except NPK₃₀₀ and NPK₁₅₀ produced taller plants than the control at all stages of growth (Table 25). The residual effect of BA₁₀₀ treatment tended to give the highest plant height of 141.9 cm which, however, did not differ significantly (p>001) from BA₁₀₀ + PM₅, BA₅₀ + PM₁₀, BA₁₀ + PM₂₀, BA₁₀₀ + NPK₇₅ and BA₅₀ + NPK₁₅₀. Minimum plant height (80.6cm) was obtained from the control.

Major variations in plant height among the treatments occurred between 4 to 8 weeks of growth. Optimum BA dose for plant height was 50tha⁻¹ while best combination was BA₅₀ + PM₁₀. It can be concluded from these results that the increase in plant height may have been due to the improvement in the nutrient status and physicochemical properties of the soil as affected by different doses of the amendments. Improvement in the soil porosity may also have contributed to better crop growth regarding shoot development in the soil and better availability of essential nutrients (Haraldsen *et al.*, 2012). The high ash dose (BA₁₀₀) may have impacted negatively on growth factors like nutrient uptake and assimilation (Sparks, 1996) which lead to reduced plant height.

Maize height (cm/plant)						
Treatment	4WAP	6WAP	8WAP	10WAP		
BA ₁₀₀	7.5	13.0	26.9	51.1		
BA ₅₀	18.3	49.5	103.2	134.7		
BA_{10}	16.3	40.8	72.7	119.2		
PM ₂₀	40.0	105.3	166.4	174.1		
PM_{10}	40.5	89.7	154.6	163.3		
PM ₅	36.6	61.9	101.1	125.1		
NPK300	15.9	50.0	100.7	158.1		
NPK150	18.7	50.4	86.1	132.0		
NPK ₇₅	16.1	42.0	63.1	103.4		
$BA_{100} + PM_5 \\$	21.7	55.1	108.7	139.3		
$BA_{50} + PM^{10}$	33.2	97.5	173.9	182.1		
$BA_{10} + PM_{20}$	41.3	105.4	187.4	189.5		
$BA_{100} + NPK_{75}$	17.7	48.1	99.9	174.8		
$BA_{50} + NPK_{150}$	22.7	68.1	135.3	168.1		
$BA_{10} + NPK_{300}$	29.5	84.5	156.5	175.5		
No amendment	12.5	26.4	41.7	71.9		
F-LSD(0.05)	4.983	12.40	19.81	23.98		

Table 24: Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on maize plant height at 4, 6, 8 and 10 weeks after planting (WAP) during the first cropping season

F-LSD_{0.05}= Fishers least significant difference at 5% level of probability.

	Maize height (cm/plant)				
Treatment	4WAP	6WAP	8WAP	10WAP	
BA ₁₀₀	35.2	78.1	123.2	141.9	
BA ₅₀	26.7	56.7	88.6	126.6	
BA ₁₀	20.1	41.5	62.8	103.1	
PM ₂₀	29.3	60.4	90.7	117.6	
PM ₁₀	27.4	47.9	72.3	109.7	
PM ₅	24.0	46.5	64.7	109.9	
NPK300	14.5	33.9	44.7	85.9	
NPK ₁₅₀	17.5	37.5	50.0	86.1	
NPK ₇₅	18.6	39.5	58.1	98.0	
$BA_{100} + PM_5$	31.4	72.1	118.5	141.2	
$BA_{50} + PM_{10}$	35.9	76.3	123.7	138.2	
$BA_{10} + PM_{20}$	32.4	65.3	97.1	130.7	
$BA_{100} + NPK_{75}$	31.1	70.4	116.11	132.4	
$BA_{50} + NPK_{150}$	27.9	61.5	92.8	128.5	
$BA_{10} + NPK_{300}$	24.1	52.0	76.2	111.2	
No amendment	15.9	35.0	46.5	80.6	
F-LSD(0.05)	4.263	8.725	14.95	13.99	

Table 25: Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10and their combinations on maize, plant height at 4, 6, 8 and 10 weeks afterplanting (WAP) during the second cropping season

F-LSD_{0.05}= Fishers least significant difference at 5% level of probability

4.7.3. Maize Stem Diameter.

The data presented in Tables 26 and 27 indicate that the treatments significantly (p<0.01) influenced the maize stem diameter in both cropping seasons. At the first cropping season, stem diameter measurement revealed that maize grown in $BA_{10} + PM_{20}$ treated plots attained the widest diameter of 4.30, 5.40, 5.0 and 5.0cm at 4, 6, 8 and 10 WAP respectively. While, those grown in BA_{100} had the least mean stem diameter of 0.37, 0.72, 1.8 and 2.4cm at 4, 6, 8 and 10 WAP respectively. The finding disagrees with Jacobson *et al.* (2000) who observed a significant increase in stem girth when using nitrogen and wood ash but small or no response to wood ash alone.

During the second cropping season, the application of BA at the rate of 100tha⁻¹ (BA₁₀₀) had the widest stem diameter of 3.2, 4.4, 3.6 and 3.5 at 4, 6, 8 and 10 WAP respectively. The least value was observed in the control plots, which had 1.1, 2.4, 2.5 and 2.5 cm at 4, 6, 8 and 10 WAP respectively.

	Stem diameter (cm/plant)				
Treatment	4 WAP	6WAP	8WAP	10WAP	
BA ₁₀₀	0.37	0.72	1.8	2.4	
BA_{50}	2.08	3.60	3.9	4.0	
BA_{10}	1.30	2.93	3.2	3.3	
PM ₂₀	3.70	5.07	4.4	4.4	
PM ₁₀	3.33	4.40	3.9	3.9	
PM ₅	2.83	3.53	3.3	3.	
NPK ₃₀₀	1.53	3.23	3.9	3.9	
NPK ₁₅₀	1.47	3.30	3.4	3.5	
NPK ₇₅	1.37	2.77	2.8	3.0	
$BA_{100} + PM_5$	2.22	3.87	4.0	4.1	
$BA_{50} + PM_{10}$	3.87	5.20	4.7	4.8	
$BA_{10} + PM_{20}$	4.30	5.40	5.0	5.0	
$BA_{100}\ +\ NPK_{75}$	1.80	3.67	3.9	4.0	
$BA_{50} + NPK_{150}$	1.93	4.43	4.4	4.4	
$BA_{10} + NPK_{300}$	2.73	5.20	4.7	4.7	
No amendment	0.98	2.00	2.3	2.6	
F-LSD(0.05)	0.6256	0.5672	0.4959	0.5090	

Table 26:Mean effects of different rates of boiler ash, poultry droppings, NPK 20:10:10and their combinations on maize stem diameter (cm) at 4, 6, 8 and 10 weeksafter planting during the first planting season

F-LSD_{0.05}= Fishers least significant difference at 5% level of probability

	Stem diameter (cm/plant)					
Treatment	4WAP	6WAP	8WAP	10WAP		
BA ₁₀₀	3.2	4.4	3.6	3.5		
BA ₅₀	2.5	3.8	3.4	3.0		
BA ₁₀	1.8	3.2	3.0	3.0		
PM ₂₀	2.4	3.6	3.3	3.2		
PM ₁₀	2.2	3.2	3.2	3.1		
PM ₅	2.0	3.1	3.0	3.0		
NPK ₃₀₀	1.4	2.5	2.5	2.5		
NPK150	1.5	2.7	2.8	2.9		
NPK ₇₅	1.6	2.7	2.9	2.9		
$BA_{100} + PM_5$	2.9	3.9	3.4	3.2		
$BA_{50} + PM_{10}$	3.0	4.2	3.4	3.3		
$BA_{10} + PM_{20}$	2.5	3.9	3.4	3.2		
$BA_{100} + NPK_{75}$	3.1	4.1	3.2	3.2		
$BA_{50} + NPK_{150}$	2.5	3.6	3.2	3.2		
$BA_{10} + NPK_{300}$	2.1	3.3	3.0	3.1		
No amendment	1.1	2.4	2.5	2.5		
F-LSD(0.05)	0.3759	0.4325	0.3875	0.3325		

Table 27: Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on maize stem diameter at 4, 6, 8 and 10 weeks after planting (WAP) during the second cropping season

F-LSD_{0.05}= Fishers least significant difference at 5% level of probability

4.7.4. Maize Leaf Number per plant.

At the first cropping season, the treatments exerted significant (p<0.01) influence on the number of maize leaves per plant. The least value (3) was obtained at 4WAP from plants grown in soils treated with BA_{100} (Table 28).While, the highest value (9.5) was obtained in plots amended with $BA_{50} + PM_{10}$, $BA_{10} + PM_{20}$, PM_{20} and PM_{10} . Similar trend was observed at 6, 8 and 10 WAP. The control plot had similar values with the other levels of BA treated plots.

Maize plants grown in PM treated plots produced higher number of leaves, which gradually increased with increase in the rate of application. Blending PM_5 with BA_{100} ($BA_{100}+PM_5$) significantly (p<0.01) reduced the number of leaves per plant by 18% while blending NPK₇₅ with BA_{100} increased it by 30% at the 4 WAP assessment. It is interesting to note that marginally irregular patterns on leaves were observed in plants grown in BA_{100} treated plots.

Assessment of leaf number at 4WAP during the second cropping season revealed that BA_{100} resulted in the highest mean number of leaves per plant (3.2) (Table29). It did not however differ from its mixtures with either PM₅ or NPK₇₅. The least value was obtained in the NPK₃₀₀ treated plot. The significant (p<0.01) effect of the amendments recorded at 4, 6 and 8 WAP could not be sustained up to the 10th week of planting (Table 29).

	Leaf number				
Treatment	4WAP	6WAP	8WAP	10WAP	
BA ₁₀₀	3.1	5.4	6.3	8.7	
BA ₅₀	6.2	10.7	13.3	13.9	
BA_{10}	5.7	9.1	10.7	12.5	
PM ₂₀	9.1	13.3	15.3	15.3	
PM_{10}	8.7	13.1	14.3	14.3	
PM ₅	8.3	11.5	13.3	14.5	
NPK ₃₀₀	6.4	10.4	13.5	14.5	
NPK ₁₅₀	6.7	10.1	11.5	13.9	
NPK ₇₅	6.1	9.1	10.5	14.3	
$BA_{100} + PM_5$	6.8	11.1	14.3	14.3	
$BA_{50} + PM_{10}$	9.5	14.3	16.1	16.1	
$BA_{10} + PM_{20}$	9.5	14.1	16.1	16.2	
$BA_{100} + NPK_{75}$	5.7	10.3	13.6	14.5	
$BA_{50} + NPK_{150}$	6.6	11.9	14.7	15.8	
$BA_{10} + NPK_{300}$	7.9	12.8	15.3	16.1	
No amendment	5.7	7.73	9.0	11.7	
F-LSD(0.05)	1.01	1.351	1.414	1.215	

Table 28 :Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10and their combinations on maize leaf number at 4, 6, 8 and 10 weeks afterplanting (WAP) during the first cropping season

F-LSD_{0.05}= Fishers least significant difference at 5% level of probability

	Leaf number				
Treatment	4WAP	6WAP	8WAP	10WAP	
BA ₁₀₀	3.2	4.4	3.6	3.5	
BA_{50}	2.5	3.8	3.4	3.0	
BA_{10}	1.8	3.2	3.0	3.0	
PM_{20}	2.4	3.6	3.3	3.2	
PM_{10}	2.2	3.2	3.2	3.1	
PM ₅	2.0	3.1	3.0	3.0	
NPK ₃₀₀	1.4	2.5	2.5	2.5	
NPK150	1.5	2.7	2.8	2.9	
NPK ₇₅	1.6	2.7	2.9	2.9	
$BA_{100} + PM_5$	2.9	3.9	3.4	3.2	
$BA_{50} + PM_{10}$	3.0	4.2	3.4	3.3	
$BA_{10}+PM_{20}$	2.5	3.9	3.4	3.2	
$BA_{100} + NPK_{75}$	3.1	4.1	3.2	3.2	
$BA_{50} + NPK_{150}$	2.5	3.6	3.2	3.2	
$BA_{10} + NPK_{300}$	2.1	3.3	3.0	3.1	
No amendment	1.1	2.4	2.5	2.5	
F-LSD(0.05)	0.3759	0.4325	0.3875	0.3325	

Table 29: Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on maize leaf number at 4, 6, 8 and 10 weeks after planting (WAP) during the second cropping season

F-LSD $_{(0.05)}$ =Fisher's Least Significant Difference at 5% level of probability.

4.7.5. Maize Leaf Area Index

The data presented in Tables 30 and 31 show that the treatments significantly (P< 0.01) influenced the maize leaf area index at all the stages of development at both cropping seasons. During the first cropping season, the leaf area index (LAI) was generally low at 4WAP but thereafter increased considerably in both the sole and combined PM treated plots up to 6WAP. Thereafter, a sharp increase was observed in all PM amended soils either sole or blended. The least LAI was obtained where BA₁₀₀ was applied alone. Blending 50tha⁻¹ BA with 150kgha⁻¹ NPK (BA₅₀ + NPK₁₅₀) was comparable to NPK₃₀₀ application. In general combined application of 10tha⁻¹ BA and 20tha⁻¹ PM (BA₁₀+PM₂₀) produced the highest LAI than application of any of sole PM or NPK.

At the second cropping season, the least LAI (0.18) at 4 WAP was measured in the 300kgha⁻¹ NPK 20:10:10 (NPK₃₀₀) treated plots and the highest from BA₅₀ + PM₁₀ and BA₁₀ + PM₂₀ plots. The trend continued until the last assessment (10WAP). The NPK₃₀₀ treated plot did not differ significantly from the control.

The high LAI observed in the PM and $BA_{10} + PM_{20}$ treated plots could be attributed to increased uptake of nutrients by the plants leading to enhanced carbohydrate synthesis which might have resulted in increased cell division and enlargement and therefore increase in the size of the leaves (Suthar, 2005). Similarly, Aronsson and Ekelund (2004) noted that since nitrogen is very low in ash, the most positive effect of wood ash application have occurred on N-rich sites or with ash amended with N-fertilizers.

	Leaf area index					
Treatment	4 WAP	6 WAP	8 WAP	10 WAP		
BA ₁₀₀	0.03	0.18	0.48	0.76		
BA_{50}	0.19	1.16	3.07	3.24		
BA_{10}	0.15	0.85	2.16	2.70		
PM ₂₀	0.82	3.97	7.00	7.00		
PM_{10}	0.74	3.57	5.95	5.95		
PM ₅	0.65	2.65	4.35	4.65		
NPK ₃₀₀	0.19	1.32	4.38	4.66		
NPK150	0.23	1.36	3.41	4.04		
NPK ₇₅	0.18	1.04	2.49	3.19		
$BA_{100} + PM_5$	0.27	1.31	3.44	3.54		
$BA_{50} + PM_{10}$	0.71	3.30	5.86	5.86		
$BA_{10} + PM_{20}$	0.18	3.97	7.40	7.32		
$BA_{100} + NPK_{75}$	0.14	0.92	2.65	2.98		
$BA_{50} + NPK_{150}$	0.24	1.65	4.20	4.53		
$BA_{10} + NPK_{300}$	0.43	2.74	5.80	6.13		
No amendment	0.10	0.46	1.06	1.61		
F-LSD(0.05)	0.1344	0.6174	1.0309	0.9920		

Table 30: Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on maize leaf area index at 4,6,8, and 10 weeks after planting (WAP) during the first cropping season

.

F-LSD (0.05) = Fisher s Least Significant Difference at 5% level of probability.

		Leaf area inc	lex			
Treatment	4 WAP	6 WAP	8 WAP	10 WAP		
BA ₁₀₀	0.62	1.93	3.56	2.97		
BA_{50}	0.42	1.30	2.43	2.20		
BA_{10}	0.35	1.04	2.08	2.10		
PM ₂₀	0.56	1.90	3.39	3.02		
PM ₁₀	0.49	1.49	2.68	2.71		
PM ₅	0.38	1.19	2.38	2.39		
NPK ₃₀₀	0.18	0.63	1.42	1.67		
NPK150	0.26	0.78	1.63	2.05		
NPK ₇₅	0.31	0.96	1.89	2.06		
$BA_{100} + PM_5$	0.46	1.65	3.30	2.84		
$BA_{50} + PM^{10}$	0.74	2.25	3.96	3.19		
$BA_{10} + PM_{20}$	0.64	1.98	3.31	3.15		
$BA_{100} + NPK_{75}$	0.49	1.52	2.77	2.32		
$BA_{50} + NPK_{150}$	0.44	1.37	2.88	2.57		
$BA_{10} + NPK_{300}$	0.41	1.21	2.28	2.27		
No amendment	0.20	0.63	1.50	1.68		
F-LSD(0.05)	0.1294	0.4007	0.6352	0.5362		

Table 31 :Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10and their combinations on maize leaf area index at 4,6,8, and 10 weeks afterplanting (WAP) during the second cropping season

TC

.

F-LSD_{0.05}= Fishers least significant difference at 5% level of probability

4.7.6. Number of Days to 50 % Maize Tasselling and Silking

Application of the treatments significantly (p<.0.01) influenced the number of days to 50% tasselling and silking of the maize plants (Table 32). The days to 50% tasselling ranged from 55 days with PM_{20} and $BA_{10}+PM_{20}$ to 79 days with BA_{100} application rate during the first cropping season. At the second cropping season, it ranged from 61 days with the BA_{100} , $BA_{100}+NPK_{75}$ and $BA_{50}+NPK_{150}$ treated plots to 74 days with the NPK_{150} application rate.

At the first cropping season, the application of BA at the rate of either 10 tha⁻¹ or 100 tha⁻¹ significantly (p<0.01) resulted in delayed maize tasselling compared to the control. However, at the second cropping season, higher rates of boiler ash resulted in early flowering compared with the control.

Maize grown in $BA_{10}+PM_{20}$ amended plots had the least number of days to 50% silking during the first cropping season. It however, did not differ significantly from PM_{20} , PM_{10} , $BA_{50}+PM_{10}$ and $BA_{10}+PM_{20}$. At the end of the second cropping, the application of boiler ash at 100 and 50tha⁻¹ significantly (p<0.01) reduced the number of days to attain 50% silking. Blending them with either PM or NPK 20:10:10 slightly reduced the number of days to 50% silking, further though not significantly.

The early tasselling and silking of maize grown on the amended plots could be attributed to increased availability and uptake of plant nutrients particularly phosphorus and potassium by the maize plant which might have resulted in fast growth and therefore early tasselling and silking. Similar findings were observed in garden egg, okra and pepper (Adeji-Nsiah and Obeng, 2013). Shahi *et al.*, (2002) also observed that increased application of nutrients particularly N, P, and K has been noted to encourage early flowering in crops.

	Days to 50% tasselling		Days to 50%	% silking	
Treatment	1 st C.S	2 nd C.S	1 st C.S	2^{nd} C.S	
BA ₁₀₀	79.0	60.7	84.0	70.0	
BA ₅₀	64.3	63.7	71.7	74.0	
BA ₁₀	68.7	70.3	77.3	81.0	
PM ₂₀	55.0	65.3	60.0	76.7	
PM_{10}	55.7	62.0	62.7	76.7	
PM ₅	60.7	67.3	69.7	81.7	
NPK ₃₀₀	66.0	69.7	76.0	81.3	
NPK ₁₅₀	66.3	73.7	78.3	81.3	
NPK ₇₅	67.0	72.0	77.3	82.7	
$BA_{100} + PM_5$	66.7	61.3	74.3	69.0	
$BA_{50} + PM^{10}$	58.3	63.0	64.3	72.7	
$BA_{10} + PM_{20}$	55.0	63.3	59.0	75.7	
$BA_{100} + NPK_{75}$	65.7	60.7	72.3	70.3	
$BA_{50} + NPK_{150}$	61.3	61.3	68.7	76.3	
$BA_{10} + NPK_{300}$	61.0	61.7	65.0	76.0	
No amendment	71.0	71.0	81.0	82.0	
F-LSD(0.05)	5.215	4.448	6.076	5.749	

Table 32: Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10):10
and their combinations on number of days to 50% tasselling and silking	

Ist C.S= First cropping season, 2nd C.S= Second cropping season, $F-LSD_{0.05}$ = Fishers least significant difference at 5% level of probability

4.7.7. Shoot Dry Weight

The shoot dry weight at 4, 8 and 12 WAP during the two cropping seasons were significantly (P<0.01) influenced by the amendments (Table 33 and 34). In the first cropping season, the biomass dry weight increased at all stages of growth and the treatment applications except BA₁₀₀. At 4WAP, biomass dry weight ranged from 1.2 to 48.3g plant⁻¹ and 0.9 to 11.6g plant⁻¹ at the first and second cropping seasons respectively. The effect of BA₁₀ + PM₂₀ on maize plant at this stage of growth during the first cropping season resulted in maximum biomass yield while the minimum was recorded with NPK₇₅. On the other hand, the evaluation of the residual effects of these amendments on dry biomass weight (Table 34) revealed that BA₅₀ + PM₁₀ had the maximum weight although it did not differ significantly from BA₁₀₀ and PM₂₀ The minimum was obtained from the NPK₇₅ treated plots.

At 8WAP during the first cropping season, the dry shoot biomass significantly(p<0.01) varied from 3.5g plant ⁻¹ for plants grown in plots amended with BA_{100} to 143.0 g plant⁻¹ in $BA_{10} + PM_{20}$ amended plots. At, a similar stage of growth during the second cropping season it ranged from 10.7g plant⁻¹ in NPK₇₅ to 72.1g plant⁻¹ in $BA_{50} + PM_{10}$.

Above ground biomass (g plant⁻¹) at the termination of the experiment (12WAP) significantly (p<0.01) ranged from 49.2 (at control) to 420.5g plant⁻¹ (at BA₅₀ + PM₁₀) during the first cropping season and 73.6 (at control) to 204.7g plant⁻¹ (at BA₁₀ + PM₂₀) in the second cropping season.

Among the BA treated plots, 50tha⁻¹ rate (BA₅₀) was superior in increasing biomass weight at the first cropping season while, the residual effect of 100tha⁻¹ (BA₁₀₀) was the highest. High application rates (100tha⁻¹) at the first cropping season lead to diminution in biomass weight. The finding was in consonance with that of Krakow (2010) who observed that the toxicity of weathered BA increased with concentration and diminished with time. Mass, 1990 and Menon et al., 1993 noted that excessive mineral salts and B content in the BA amended soil were found to be the major contributory factors for the observed plant mortality and biomass reduction. This study is also consistent with the findings of Adriano *et al.* (1980) and Sharma *et al.* (2011). The inability of the plants grown in 100tha⁻¹ BA treated plots to survive up to 2-4weeks may be due to ambient heat (induced drought stress) coupled with the risk of metal toxicity (Gupta *et al.*, 2002; Ansari *et al.*, 2011).

	Dry Shoot Biomass (g/plant)			
Treatment	4 WAP	8 WAP	12 WAP	
BA ₁₀₀	3.6	3.5	90.5	
BA_{50}	7.9	64.3	274.8	
BA_{10}	4.8	84.7	155.5	
PM ₂₀	40	134.7	363.8	
PM ₁₀	43.2	116.7	264.9	
PM ₅	15.9	79.7	140.1	
NPK ₃₀₀	3.6	78.7	209.9	
NPK150	2.7	56.7	149.3	
NPK ₇₅	3.7	48.7	92.5	
$BA_{100} + PM_5 \\$	12.3	98.7	341.8	
$BA_{50} + PM_{10}$	29.2	125.3	420.5	
$BA_{10}+PM_{20}$	48.3	143.0	400.1	
$BA_{100} + NPK_{75}$	5.1	94.3	270.1	
$BA_{50} + NPK_{150}$	10.6	91.3	281.9	
$BA_{10} + NPK_{300}$	11.0	165.0	307.4	
No amendment	1.2	15.3	49.2	
F-LSD(0.05)	19.11	62.35	79.14	

Table 33: Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on maize dry shoot biomass (g plant ⁻¹) at 4,8, and 12 weeks after planting (WAP) during the first cropping season

F-LSD (0.05) =Fisher's Least Significant Difference at 5% level of probability.

	Dry Shoot Biomass (g plant ⁻¹)				
Treatment	4 WAP	8 WAP	12 WAP		
BA100	10.5	51.1	184.5		
BA_{50}	6.4	36.6	164.6		
BA_{10}	5.0	15.6	129.1		
PM ₂₀	10.0	36.3	162.3		
PM ₁₀	7.9	26.4	120.6		
PM ₅	3.9	15.8	119.2		
NPK ₃₀₀	14.2	10.7	84.8		
NPK ₁₅₀	0.9	13.2	91.2		
NPK ₇₅	8.0	23.9	84.6		
$BA_{100} + PM_5$	8.7	71.1	204.7		
$BA_{50} + PM_{10}$	11.6	72.1	226.9		
$BA_{10} + PM_{20}$	8.7	49.2	168.5		
$BA_{100} + NPK_{75}$	7.8	52.2	182.5		
$BA_{50} + NPK_{150}$	6.1	58.9	169.4		
$BA_{10} + NPK_{300}$	5.9	37.2	109.0		
No amendment	3.0	12.3	73.6		
F-LSD(0.05)	4.096	24.30	43.39		

Table 34 : Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10and their combinations on maize dry shoot biomass (g/plant) at 4,8, and 12weeks after planting (WAP) during the second cropping season

F-LSD (0.05) =Fisher's Least Significant Difference at 5% level of probability.

Although the use of poultry droppings substantially increased biomass yield between 4 to 8 WAP, successive increase in manure rate from 10-20tha⁻¹ did not produce any significant effect except at 12WAP. Agba *et al.* (2012) obtained similar findings. Integrated application of BA and PM was generally superior in increasing biomass weight. For instance, the application of BA₅₀ + PM₁₀ increased plant biomass by approximately nine-folds compared to the control at the first cropping season and 3-folds at the second cropping season.

Increase in shoot biomass weight as a result of the application of the amendments may be attributed to a balanced nutrient uptake by the maize plants (Wange and Kale; 2004) which resulted in enhanced cell division and enlargement (Prabhu *et al.* 2003) leading to shoot growth and development. The fertility status of the soils which was improved by the addition of these amendments might have aided nutrient acquistion in the plant parts thus increased biomass content of the whole plant. Khan and Khan (1996) found that tomato plants responded positively to flyash (FA) soil amendment showing luxirant growth up to 60 or 70% and above which it had a deleterious effect. Lal (1999) attributed the better growth of soybean in a 16% FA amended soil to the presence of utilisable plant nutrients in FA. Ghuman *et al.* (1994) revealed that addition of FA improved the dry weight and yield of Zea mays. Similarly, Selvakumari et al. (2000) noted that increased straw and grain yield in FA amended plot was due to better supply of nutrients, conducive physical environment leading to better aeration, root activity and nutrient absorption and the consequent complementary effect.

Invariably, the highest BA concentration (BA₁₀₀) adversely affected the plant metabolism vis-à-vis its growth which might be attributed to higher concentration of heavy metals in the system leading to toxic effect (Sushil and Batra; 2006). In this study, there was retarded root growth of maize plants grown in soils amended with BA₁₀₀ ,although not shown. Gunse *et al.* (2000) reported that root growth inhibition might be due to high contents of heavy metals like Cu, Cd, Zn e.t.c which inhibited root enlongation by reducing cell division. The retardation of the overall performance of the BA₁₀₀ treatment may have affected the basic photosynthetic tools. This observation is consistent with the findings of Adriano *et al.* (1980) and Sharma *et al.*; (2011). It would therefore appear that the use of BA alone at excessive rates has the potential to restrict the plant growth possibly by modifying soil pH and soil nutrient supply. The study also suggest that it is better to use integrated BA and PM mixtures than sole BA or PM and the mixture should not be applied at rates greater than 50tha⁻¹ BA even when designed as a single application.

4.7.8. Maize Growth Rate Estimates

Growth rates based on changes in shoot dry weight between 4 and 8 weeks and between 8 and 12 weeks after planting for the two cropping seasons are shown in Table 35 and 36. Application of BA up to 50tha⁻¹ increased plant growth rate (PGR) but PGR was reduced significantly when the ash was applied at 100tha⁻¹. In the contrary, higher doses of PM and NPK 20:10:10 fertilizer had higher plant growth rates. Sole application of BA₁₀, PM₂₀, PM₁₀ and NPK₃₀₀ and all their integrated doses increased PGR significantly (p<0.01) relative to the control.

At the second cropping season, it was only BA_{100} and all integrated doses except BA_{10} + NPK₃₀₀ that significantly influenced the PGR relative to the control. At the period between 8 to 12 WAP, PGR was largely insensitive to application of the amendments at both cropping seasons. The amendments did not significantly influence the relative growth rate in both cropping seasons.

The differential effects of the amendments on PGR may be largely attributed to their salinity and nutrient composition (Table 6). Tester and Devenport (2003) observed that high concentration of salts in soil solution interferes with uptake of water by the roots and balanced absorption of essential nutritional ions by plants. In general, salt stress decreases the photosynthesis and respiration rate of plants (Jouyban, 2012). The osmotic stress results to stomatal closure, decline in photosynthesis and occurrences of photo inhibition and oxidative stress leading to inhibition of cell expansion either directly or indirectly through abscisic acid. The low plant growth rate (PGR) recorded when the ash was applied at 100 tha⁻¹ may be in tandem with the findings of Yunusa et al.,(2008) who observed that relative chlorophyll concentration was reduced only when canola was supplied with more than 125 Mg ha⁻¹ of gray ash. The insensitivity of the amendments on PGR at the period between 8 to 12WAP may be attributed to the leaching effect of the salt by water.

Growth Rate					
Treatment	4-8 WAP	8-12 WAP	Relative growth rate		
BA100	0.1	193	2.3		
BA_{50}	47.1	815	18.3		
BA ₁₀	66.6	840	29.5		
PM ₂₀	78.9	1732	2.0		
PM ₁₀	61.2	823	1.7		
PM ₅	531	340	71.7		
NPK300	62.6	690	18.9		
NPK ₁₅₀	44.9	413	26.5		
NPK ₇₅	38.1	360	6.8		
$BA_{100} + PM_5$	72.0	1693	7.5		
$BA_{50} + PM_{10}$	80.1	1667	2.9		
$BA_{10}+PM_{20}$	78.9	1263	2.1		
$BA_{100} + NPK_{75}$	74.4	673	18.1		
$BA_{50} + NPK_{150}$	67.3	178	19.3		
$BA_{10} + NPK_{300}$	128.3	548	32.8		
No amendment	11.8	1160	10.7		
F-LSD _(0.05)	45.81	n.s	n.s		

Table 35: Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on maize growth rate and relative growth rate during the first cropping season

~

F-LSD (0.05) =Fisher s Least Significant Difference at 5% level of probability, n.s = nonsignificant at 5% probability level.

	Growth Rate			
Treatment	4-8 WAP	8-12 WAP	Relative growth rate	
BA ₁₀₀	34.2	626	3.70	
BA_{50}	25.2	922	3.85	
BA_{10}	8.9	484	1.48	
PM ₂₀	21.9	485	2.23	
PM ₁₀	15.4	644	2.32	
PM ₅	9.9	546	3.16	
NPK ₃₀₀	5.4	358	1.82	
NPK ₁₅₀	10.3	240	12.44	
NPK ₇₅	13.2	352	2.84	
$BA_{100} + PM_5$	52.0	460	5.91	
$BA_{50} + PM_{10}$	50.4	816	4.21	
$BA_{10} + PM_{20}$	33.7	798	4.12	
BA ₁₀₀ + NPK ₇₅	37.1	503	4.78	
$BA_{50} + NPK_{150}$	44.0	763	8.71	
$BA_{10} + NPK_{300}$	26.1	216	5.47	
No amendment	7.7	146	2.66	
F-LSD(0.05)	19.89	n.s	5.442	

Table 36:_Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on maize plant growth rate and relative growth rate during the second cropping season

F-LSD (0.05) =Fisher's Least Significant Difference at 5% level of probability, ns=non- significant at 5% level of probability.

4.8. Grain Yield and Yield Components.

4.8.1. Average Maize Cob Weight per Plant.

The weight of cob per plant was very highly significantly (P<0.01) influenced by the treatments at both cropping seasons (Table 37). In the first cropping season, the highest yield of 142g cob⁻¹ was from the plots treated with $BA_{10} + PM_{20}$. This was, however, statistically the same with that obtained from plants grown in plots amended with PM_{20} , PM_{10} and $BA_{50} + PM_{10}$. The lowest cob weight (23g cob⁻¹) was obtained from BA_{100} treated plots.

During the second cropping season, the heaviest cob weight (68g) was obtained from the plot that received PM_{20} the previous year. It was however statistically the same with plots amended with $BA_{10} + PM_{20}$, PM_{10} , PM_5 , BA_{100} , PM_5 and $BA_{50} + PM_{10}$. The lowest (25g) obtained from $BA_{10} + NPK_{300}$ treated plot was statistically the same with the rest of the treatments.

At both cropping seasons, there were non-significant differences among the BA rates while the cob weight increased linearly with increase in the rate of poultry droppings. With exception of residual BA_{10} +NPK₃₀₀, blending BA with different levels of NPK 20:10:10 did not significantly increase the cob weight. The high cob weight in the PM based treatments may be related to the high nitrogen content of the amendment and the content of balanced nutrients.

4.8.2. Maize Grain Yield (tha⁻¹)

Maize grain yield (tha⁻¹) was very highly significantly (P<0.01) influenced by the type and quantity of amendment applied (Table 37). Boiler ash application did not significantly increase grain yield at both cropping seasons relative to the control. Among the BA treated plots, the lowest dose (10tha⁻¹) consistently had the highest grain yield at both cropping seasons. The result agrees with that of Haraldsen *et al.* (2012) who found that when bottom wood ash was applied without sufficient N supply, the effect on crop growth and yield is minimal and the plants did not take up the potential plant nutrients supplied. The result, however, contrasted the findings of several authors (Jamil et al. 2004; Khan and Quasim, 2008; Ram *et al.*, 2011; Ezema *et al.*, 2013) who reported that BA increases crop yield significantly at rates between 25 to 60 tons per hectare. However, it is worthy to note that in

	Cob yie	Cob yield /plant		$t (tha^{-1})$	% yield reduction
Treatment	I st C.S	2 nd C.S	I st C.S	2 nd C.S	_
BA100	23.1	34.5	0.58	.077	-32.8
BA_{50}	52.5	30.0	1.39	0.64	54.0
BA_{10}	46.5	32.4	1.50	0.95	36.7
PM ₂₀	141.1	67.5	5.67	2.56	54.9
PM_{10}	102.5	48.9	4.01	1.91	52.4
PM ₅	51.7	51.0	1.90	1.87	15.8
NPK ₃₀₀	73.4	36.0	2.52	1.22	51.6
NPK ₁₅₀	39.3	38.2	1.36	1.48	-10.0
NPK ₇₅	36.8	37.7	1.36	1.37	-7.4
$BA_{100} + PM_5$	88.1	46.6	2.41	0.88	63.5
$BA_{50} + PM^{10}$	124.8	52.5	4.37	1.35	69.1
$BA_{10} + PM_{20}$	142.9	65.5	5.43	2.38	56.2
$BA_{100} + NPK_{75}$	48.1	25.2	1.19	0.34	71.4
$BA_{50} + NPK_{150}$	47.6	35.7	1.06	0.77	27.4
$BA_{10} + NPK_{300}$	72.3	27.4	2.62	0.93	64.5
No amendment	25.1	27.9	0.86	1.12	-30.2
F-LSD(0.05)	36.78	22.94	1.446	0.927	7.54

Table 37: Mean effect of different rates of boiler ash, poultry droppings, NPK 20:10:10and their combinations on maize cob yield (g cob⁻¹) and maize grain yield (tha⁻¹)

 1^{st} C.S= first cropping season, 2^{nd} C.S= second cropping season, F-LSD_{0.05}= Fishers least significant difference at 5% level of probability

most of these studies that reported increased yield of crops following application of BA, basal doses of NPK fertilizer or urea was applied.

The use of PM produced more vigorous maize plants having significantly (P<0.01) higher cob weights. Thus, the highest maize grain yields of 5.67 and 2.56tha⁻¹ were obtained in plots amended with 20 tha⁻¹ PM at the first and second cropping seasons respectively. However, the yield was similar to that obtained from plots that received a blend of 50 tha⁻¹ BA and 10 tha⁻¹ PM. The recommended NPK 20:10:10 fertilizer rate for maize (NPK₃₀₀) had significantly (P<0.01) higher yields than the unfertilized plots at the first cropping season. The residual effect however, revealed non-significant difference relative to the control. The grain yield obtained from plots amended with lower rates (NPK₁₅₀, NPK₇₅) did not significantly differ with that of the control.at both cropping seasons.

A yield advantage was observed due to combined application of BA with low levels of PM and all levels of NPK 20:10:10 in both cropping seasons. The integrated fertilization treatments including BA and PM or NPK 20:10:10 were superior to all levels of NPK 20:10:10 and low level of PM. Similar findings have been reported by Selvakumari *et al.* (1999), Rautaray *et al.* (2003) and Ram *et al.* (2007). They noted that integration of fly ash with organic (farmyard manure) or inorganic (NPK,urea) fertilizers, because of synergistic effects resulted in better nutrient uptake, higher yield and improved maintenance of soil fertility. In this study, synergism occurred only when low doses of BA was blended with low levels of PM or low levels of BA and high doses of NPK-fertilizer. The most synergistic effect of blending BA with either PM or NPK-fertilizer was observed with the lowest rate of BA (BA₁₀). This implies that the inclusion of BA in the amendments at high application rate did not affect the maize grain yield significantly.

It can be inferred from the results that the high N poultry droppings amendments supported higher yield than NPK-fertilizer and BA. In this study, it was also observed that the BA significantly (p<0.01) increased maize growth parameters, but grain yield was low probably due to unbalanced nutrition in the BA amended plots. The non-significant effect of BA application on maize grain yield may be because of low N in both the soil and the BA (Table 3 and 6). It may also be attributed to probable high salinity caused by high levels of sulphate, chloride, carbonates and bicarbonates in the BA amended soils (Singh and Siddiqui, 2003). The superior impact of PM over NPK-fertilizer agrees with Sanwal *et al.* (2007). They observed that

despite, the large quantities of plant nutrients contained in NPK-fertilizer as compared to organic nutrients, the presence of growth promoting agents in organic fertilizers such as plant growth promoting rhizobacteria (PGPR), amino acids, growth hormones etc, make them important for enhancement of soil fertility and productivity. The application of BA and PM might have resulted in increased microbial activity in the soil and increased organic matter production with its concomitant increased availability of nutrients such as N, P and K (Saarsalmi *et al.*, 2001; Ojeniyi *et al.*, 2010).

The percentage yield reduction from the first cropping season (time of amendment application) and the second cropping season (residual effect of amendment) was significantly (p<0.01) influenced by the amendments (Table 37). Highest yield reduction was observed in $BA_{100} + NPK_{75}$ while the least was observed in the control. The lower maize grain yield at the second cropping season may be attributed to the exhaustion of soil nutrients through uptake by the maize plants at the first cropping season as evidenced by the higher dry shoot biomass weights.

Generally, the grain yield may have been influenced by the cumulative effect of the plants vegetative growth such as number of leaves, plant height and stem girth and to the level of balanced nutrition supplied to the plants by the ammendments. These may have lead to effective photosynthesis and distribution of the carbohydrate that resulted in the higher amount of grains in amended plots.

4.8.3. Harvest Index of Maize

The harvest index which is the physiological efficiency of the maize crop to partition the dry matter into economic (grain) yield was significantly (P<0.05) influenced by the application of the soil amendments in both cropping seasons. A low harvest index indicates a low efficiency of translocation of assimilates (Lucas, 1984). The results of the first cropping season indicate that $BA_{50} + NPK_{150}$ had the least harvest index value of 0.009. It was, however, statistically the same with BA_{100} , BA_{50} , BA_{10} , NPK_{150} , $BA_{100}+NPK_{75}$ and $BA_{100}+PM_5$ (Table 38). It also showed that PM_{20} had the highest harvest index (0.329) which however did not differ significantly from the control and the rest of the other amendments.

At the second cropping season, the comparison of treatment means showed that BA_{100} , BA_{50} , $BA_{100} + PM_5$, $BA_{100} + NPK_{75}$ and $BA_{50} + NPK_{150}$ significantly (P<0.05)
	100-grai	n weight (g)	Harves	t index
Treatment	1 st C.S	2 nd C.S	1 st C.S	2 nd C.S
BA100	22.7	25.83	0.114	0.083
BA_{50}	31.5	20.63	0.080	0.070
BA_{10}	21.1	24.40	0.150	0.148
PM ₂₀	30.2	26.43	0.329	0.296
PM ₁₀	25.2	23.17	0.274	0.276
PM ₅	18.9	21.90	0.233	0.271
NPK ₃₀₀	19.9	18.30	0.220	0.234
NPK ₁₅₀	21.6	20.03	0.143	0.228
NPK ₇₅	13.8	18.42	0.304	0.358
$BA_{100} + PM_5$	30.1	23.13	0.120	0.070
$BA_{50} + PM_{10}$	28.3	24.25	0.189	0.116
$BA_{10} + PM_{20}$	32.6	26.50	0.262	0.255
$BA_{100} + NPK_{75}$	23.0	23.40	0.088	0.031
$BA_{50} + NPK_{150}$	23.3	27.87	0.009	0.065
$BA_{10} + NPK_{300}$	25.3	19.91	0.175	0.155
No amendment	11.6	19.63	0.246	0.229
F-LSD(0.05)	6.495	n.s	0.1492	0.1334

Table 38: Effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on 100-grain weight and harvest index of maize

 1^{st} C.S= first cropping season 2^{nd} C.S= second cropping season, n.s= non-significant at 5% level of probability,F-LSD_{0.05}= Fishers least significant difference at 5% level of probability

reduced the harvest index relative to the control.. The highest harvest index value (0.358) obtained in plots treated with NPK₇₅ was, however, statistically the same with the control and the rest of the other treatments. The finding was contrary to that of Farhad *et al.*, 2009; Amanullah *et al.*, 2014 and Yolou *et al.*, 2015 which observed that organic manure (poultry droppings and compost) had higher harvest index than NPK fertilizer..

4.8.4. 100-grain weight (g) of Maize

The data in Table 38 revealed a significant (P<0.01) increase in 100-grain weight of maize in all the amended plots over the control in the first cropping season. The highest 100-grain weight (32.6g) was found in the treatment receiving $BA_{10} + PM_{20}$ which incidentally had the highest grain yield. It was statistically the same with BA_{50} , PM_{20} , $BA_{100} + PM_5$ and $BA_{50} + PM_{10}$. It was obvious from the data that all the treatments getting different rates of BA except BA_{50} were statistically the same with each other and with all the mineral fertilizer treatments. The result agrees with that of Kalra *et al.* (1998) who reported that 1000 grain weight in bagasse ash treatments increased significantly over the control due to the availability of P and micro nutrients like Zn and Cu.

The second cropping data presented in Table 38 revealed a non-significant increase in the 100-grain weight among the treatments and the control. A possible reason could be that most of the nutrients contained in the amendments were released during the first cropping season.

4.8.5 Sustainable Yield Index (SYI) and Agronomic Efficiency (AE) of Maize

The sustainable yield index (SYI) as influenced by the different amendments is presented in Table 39. It was greater in all the plots under the poultry droppings treatment. Lower values of SYI were recorded in the second cropping season than in the first. The findings agree with Efthimiadou *et al.* (2010) in sweet maize production using combined organic/inorganic treatment. It may be inferred from the SYI data that maize crop yield is more stable under BA_{10} and PM fertilization treatments compared with inorganic fertilization. Bhattacharayga et al. (2008) observed similar result in a soybean-wheat cropping system.

Among the various treatments analyzed, application of BA_{10} without PM or mineral fertilizer sustained AE in the first cropping season while in the second cropping season, it

Sustainable Yield	Index(SYI)		Agronomic E	fficiency (AE)
Treatment	1 st C.S	2^{nd} C.S	1 st C.S	2^{nd} C.S
BA100	-0.072	-0.069	-2.16	-0.45
BA ₅₀	0.003	-0.086	10.97	-2.98
BA ₁₀	-0.043	0.038	26.6	-2.45
PM ₂₀	0.651	0.386	7.87	1.87
PM_{10}	0.369	0.254	9.20	2.17
PM ₅	0.097	0.268	5.47	4.19
NPK ₃₀₀	0.180	-0.143	4.58	0.49
NPK ₁₅₀	0.025	0.051	2.8	2.10
NPK ₇₅	-0.059	0.032	0.89	3.28
$BA_{100} + PM_5 \\$	0.080	-0.333	5.88	-0.26
$BA_{50} + PM_{10}$	0.411	-0.082	9.81	0.66
$BA_{10} + PM_{20}$	0.612	0.323	7.19	1.61
$BA_{100} + NPK_{75}$	-0.120	-0.022	1.05	0.149
$BA_{50} + NPK_{150}$	0.023	-0.130	2.09	0.0.66
$BA_{10} + NPK_{300}$	0.247	-0.005	6.68	-0136
No amendment	-0.144	-0185	-	-

Table 39: Sustainable yield index (SYI) and agronomic efficiency (AE) of maize grown in soil amended with different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations

 $SYI = (Y_m - Sd)/Ymax$

 $AE = (Y_1 \circ Y_0) / F_0$

Where Ym = Mean Yield

Sd = Standard deviation

Ymax = Maximum yield obtained under a set of management practice.

 Y_1 = Grain yield in treated soil in each phase of the study

,

 $Y_o = Grain$ yield in control plot

 F_o = Amount of nitrogen applied expressed in the same unit

was PM_5 . In the first cropping season, AE was higher in the plots treated with PM. Similar to SYI; lower values of AE were also recorded at the second cropping season than in the first. Integration of 50 tons of BA with 10 tons of PM, and 10 tons of BA with 20 tons of PM had higher AE among the combined rates of the amendments at first and second cropping seasons respectively.

4.8.6. Concentration of Nutrients in Maize Grains

The concentration of nutrients in maize grains was significantly (P<0.01) affected by the different fertilization treatments (Table 40). Average N concentration across all treatments was 1.41 mg kg⁻¹ in the first cropping season and decreased to 0.62 mg kg⁻¹ in the second cropping season. The nitrogen content of the maize grains ranged from 0.91 mg kg⁻¹ (BA₁₀ + NPK₃₀₀) to 2.13 mg kg⁻¹ (BA₁₀₀) and 0.14 (NPK₁₅₀) to 1.04 mg kg⁻¹ (BA₁₀₀) during the first and second seasons respectively. The BA₁₀₀ treatment had the highest value in both cropping seasons. There were significant (P<0.01) increase in N concentration of grains harvested in BA₅₀, PM₂₀, PM₁₀, NPK₁₅₀, BA₁₀₀ + PM₅, BA₅₀ + PM₁₀, BA₁₀₀ + NPK₁₅₀ treated plots relative to the control.

In this study, all maize grains harvested at the first cropping season had low P content and did not differ significantly from each other (Table 40). However, at the second cropping season it increased remarkably. Highest value (0.82 mgkg⁻¹) was recorded in PM₅ while the minimum (0.21 mgkg⁻¹) was from the control plots. The reason for the increase is not clear, as it was observed in all treatments. This suggests that it may be related to climatic conditions as opposed to particular characteristics of individual treatment.

Potassium content of maize grain was significantly (P< 0.05) influenced by the treatment at the first cropping season (Table 40). It ranged from 47.9 mgkg⁻¹ in the control plots to 96.1 mgkg⁻¹ in BA₁₀ +NPK ₃₀₀ treated plots. The maize grains obtained from BA₁₀ + NPK ₃₀₀ was statistically the same with grains obtained from BA₅₀ + PM₁₀ and BA₁₀ + PM₂₀. Sole application of the amendments did not significantly increase the K uptake relative to the control. The residual effect of the amendments did not manifest any significant influence.

The sulphur concentration of the maize grains was significantly (p<0.01) affected by the amendments at both cropping seasons (Tables 40 and 41). Comparative analysis showed

			Nutrient cond	centrations in ma	nize grain
	%	ííí	ííí mg kg ⁻¹	ííííííí	
Treatment	N	Р	K	Na	S
BA ₁₀₀	2.3	0.3	78.57	28.56	0.11
BA ₅₀	1.6	0.4	87.62	28.42	0.120
BA ₁₀	1.27	0.3	58.72	27.73	0.116
PM_{20}	1.56	0.3	68.64	23.14	0.136
PM_{10}	1.52	0.3	58.79	21.39	0.120
PM ₅	1.14	0.4	78.52	22.75	0.142
NPK ₃₀₀	1.12	0.3	58.15	18.59	0.134
NPK150	1.55	0.6	48.80	17.47	0.128
NPK ₇₅	1.12	0.	47.88	18.46	0.133
$BA_{100} + PM_5$	1.69	0.4	48.57	29.42	0.125
BA50 +PM10	1.45	0.4	95.62	17.32	0.135
$BA_{10}+PM_{20} \\$	1.27	0.5	94.63	28.37	0.145
$BA_{100}\ +\ NPK_{75}$	1.13	0.6	58.66	17.85	0.120
$BA_{50} + NPK_{150}$	1.59	0.8	78.85	20.07	0.133
$BA_{10} + NPK_{300}$	0.91	0.6	96.09	18.86	0.135
No amendment	1.40	0.6	78.4	17.62	0.134
F-LSD(0.05)	0.0293	n.s	7.665	2.218	0.0018

Table 40: Effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on nutrient composition of maize grains during the first cropping season

n.s= non-significant at 5% level of probability, F-LSD_{0.05}= Fishers least significant difference at 5% level of probability.

Nutrient concentrations in maize grain								
	%	íííí	í í (mg kg ⁻¹) íííííí	í .			
Treatment	N	Р	K	Na	S			
BA_{100}	1.04	0.64	0.09	0.045	1.07			
BA_{50}	0.74	0.55	0.08	0.055	0.94			
BA_{10}	0.74	0.054	0.08	0.045	1.15			
PM_{20}	0.74	0.66	0.09	0.045	1.31			
PM_{10}	0.15	0.55	0.11	0.035	0.92			
PM ₅	0.89	0.82	0.10	0.055	1.23			
NPK ₃₀₀	0.91	0.69	0.10	0.045	1.26			
NPK ₁₅₀	0.14	0.35	0.09	0.055	0.97			
NPK ₇₅	0.15	0.44	0.11	0.075	0.93			
$BA_{100} + PM_5$	0.66	0.22	4.54	0.055	1.32			
$BA_{50} + PM^{10}$	0.71	0.23	0.08	0.055	1.06			
$BA_{10} + PM_{20}$	0.92	0.45	0.08	0.045	1.01			
BA ₁₀₀ + NPK ₇₅	0.72	0.51	0.09	0.045	1.43			
$BA_{50} + NPK_{150}$	0.18	0.46	0.09	0.055	1.54			
$BA_{10} + NPK_{300}$	0.62	0.42	0.09	0.045	0.96			
No amendment	0.70	0.21	0.09	0.050	0.84			
F-LSD(0.05)	0.095	0.0698	n.s	0.0038	0.0477			

Table 41: Effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combination on maize grain nutrient composition of during the second cropping season

n.s= non-significant at 5% level of probability, $F-LSD_{0.05}$ = Fishers least significant difference at 5% level of probability

that grain sulphur concentration in the $BA_{10} + PM_{20}$ treatment was the highest (0.145 mgKg⁻¹), while the least was recorded in BA_{100} plots which had the highest N concentration. At the second cropping season, Sulphur content of maize grains ranged from 0.84 (control) to 1.54 mgkg⁻¹ (BA₅₀ + NPK ₁₅₀).

A significant variation in sodium concentration in maize grains was recorded due to the application of the different treatment at the two cropping season. Maize grains from the first cropping harvest in plots amended with BA exhibited high Na concentration than that from PM and NPK .The NPK 20:10:10 treated plots were generally low in maize Na concentration. At the second cropping season, the Na content was dramatically reduced. It ranged from 0.035 (PM_{10}) to 0.075 mgkg⁻¹ (NPK ₇₅).

The uptake of nutrients and their distribution to different parts of the maize plant have been found to vary primarily with the fertility of the soil (Ologunde, 1974). The increase in nutrient concentration of maize in this study might be associated with the positive effects of the amendments in increasing the water use efficiency and photosynthetic activity, which directly affect physiological processes.

It is apparent from Tables 40 and 41 that sole application of BA at high application rates resulted in higher uptake of N, K and Na than application of PM or NPK 20:10:10. The uptake of K and S was higher under integrated nutrient treatment involving $BA_{10} + NPK_{300}$ than application of only BA. The higher nutrient uptake under these treatments was not reflected in their maize grain yield. Contrary findings have been reported (Sarangi *et al.* 1997, Rautaray *et al.* 2003).

4.8.7. Maize Grain Concentration of Heavy Metals

Average concentrations of boron, cadmium and zinc in maize grains harvested at both cropping seasons are presented in Table 42. Treatment and cropping seasons effects had significant impact on the concentration of these metals in the maize grains. Boron concentration in maize grain was significantly (p<0.05) influenced by the treatments at both cropping seasons. In the first cropping season it was highest (14.35 mgkg⁻¹) in grains harvested from the plot treated with BA₁₀₀ + NPK₇₅, followed by BA₁₀ + PM₂₀ and BA₅₀ + PM₁₀,while the least was obtained from BA₁₀₀ treated plots. During the second cropping season, the highest (3.62 mgkg⁻¹) was obtained from grains grown in plots treated with

Treatment	Boron	Cadmium	Zinc
	íííííííí	(mg kg ⁻¹)í í í í	ÍÍÍ
BA100	0.77	0.034	13.0
BA_{50}	9.55	0.039	7.5
BA_{10}	4.77	0.043	7.0
PM_{20}	11.58	0.045	5.5
\mathbf{PM}_{10}	5.95	0.023	10.5
PM ₅	9.45	0.034	5.6
NPK ₃₀₀	7.33	0.037	5.4
NPK150	10.44	0.037	6.6
NPK ₇₅	8.34	0.036	4.6
$BA_{100} + PM_5$	11.85	0.042	12.0
$BA_{50} + PM_{10}$	13.06	0.049	6.1
$BA_{10} + PM_{20}$	13.11	0.039	6.7
$BA_{100} + NPK_{75}$	14.35	0.044	6.2
$BA_{50} + NPK_{150}$	11.83	0.039	5.4
$BA_{10} + NPK_{300}$	11.63	0.041	6.1
No amendment	8.34	0.002	11.5
F-LSD(0.05)	0.1886	0.035	1.184

Table 42: Effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on heavy metal concentration in maize grains during the first cropping season

n.s= non-significant at 5% level of probability, F-LSD_{0.05}= Fishers least significant difference at 5% level of probability

Treatment	Boron	Cadmium	Zinc				
	ííííí	íííííííí. (mg kg ⁻¹)ííííííí.					
BA ₁₀₀	2.42	3.12	5.3				
BA ₅₀	1.13	3.32	3.1				
BA_{10}	1.17	3.24	2.7				
PM ₂₀	1.10	3.24	2.3				
PM ₁₀	1.1	4.7	4.7				
PM ₅	1.20	4.29	2.1				
NPK ₃₀₀	3.56	4.33	4.6				
NPK ₁₅₀	3.62	2.47	2.7				
NPK ₇₅	2.55	3.74	2.1				
$BA_{100} + PM_5$	2.39	3.82	4.7				
$BA_{50} + PM^{10}$	1.08	2.72	2.7				
$BA_{10} + PM_{20}$	1.06	3.93	2.7				
$BA_{100} + NPK_{75}$	1.10	4.53	2.5				
$BA_{50} + NPK_{150}$	0.94	2.84	2.2				
$BA_{10} + NPK_{300}$	1.21	2.84	2.7				
No amendment	1.20	2.18	4.7				
F-LSD(0.05)	0.1488	0.0783	0.2806				

Table 44: Effect of different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations on heavy metal concentration in maize grains during the second cropping season

 $F-LSD_{0.05}$ = Fishers least significant difference at 5% level of probability

 NPK_{150} which was statistically the same with NPK_{300} plots. The least value was obtained from $BA_{50} + NPK_{150}$ treated plots.

Among the BA treated plots, B concentration in maize grains obtained from BA_{50} treated plots increased significantly (p<0.05) over other sole BA treatments and the control in the first cropping season. In the second cropping season it was the BA_{100} rate. Overall boron concentration decreased drastically from the first to the second cropping season.

Cadmuim concentrations in the grains harvested from all treated plots were higher in the second cropping season than in the first cropping season. At the first cropping season, the highest Cd concentration was obtained in the plants grown on the $BA_{50} + NPK_{150}$ treated plot while the lowest value was recorded in BA_{10} . Samples from both the treated plots and control were below 0.05mgkg⁻¹. Patterson (2001) noted that since they were below the detection limit of 1 mgkg^{-1} they did not warrant further statistical comparison among samples.

Mean cadmium content of the grains from second seasons harvest was statistically (p<0.05) higher in samples obtained from plots amended with $BA_{100} + NPK_{75}$ and lowest in the control. All treatments significantly increased cadimum content of the maize grains relative to the control. Among the sole BA treatments, BA_{50} had significantly higher value than others. It is interesting to note that lower accumulation of cadmium was observed in the soil compared to the maize grain regardless of the source of fertilizations. This result indicates that cadmium accumulation in grains should be of concern.

Zinc content in grains harvested at the first cropping season from plots amended with BA_{100} had the highest value of 13.0 mgkg⁻¹. It was statistically the same with $BA_{100} + PM_5$. The least value was observed in NPK₇₅. Similar trend was obtained at the second cropping season. Average Zn concentration across all treatments was 7.47 mgkg⁻¹ in the first cropping season and decreased to 3.24 mgkg⁻¹, the following year. The observed decrease is potentially the result of the stabilization of the organic matter in the biosolid fraction of the amendments. Metal uptake by plants in biosolid amended soils is generally highest in the first year following application (Logan and Chaney, 1983, Brown *et al.* 2003). It is important to note that despite the high total plant Zn concentration in all treatments that included BA, they were below levels associated with Zn toxicity (Chaney, 1993).

The presence of trace amounts of elements of environmental concerns in the BA was not of much concern. This may be attributable to the alkaline nature of the ash and associated impact of its application with organic substrates (PM), which help in the controlled carryover of these elements, besides the accompanying dilution of these elements due to enhancement in the yield of crop products. None of the elements demonstrated that their concentration traversed permissible limits at 10 and 50 tha⁻¹ of BA addition. Although, cadmium and zinc didnøt reach up to phytotoxic level in any rate but phytotoxicity symptoms were noticed at 100tha⁻¹ rate addition viz. decline in growth parameters.

4.8.8. Metal Bio concentration Factor (BCF)

The bio-concentration factor of heavy metals in maize grains as influenced by the different amendments (Table 44) were in the order B > Zn > Cd at the first cropping season, while at the second cropping season, the order was Cd > Zn > B. The BCF of boron and zinc was found to be high (Table 44) at the first cropping season while that of cadmium was higher at the second cropping season. Thus, the study indicates that heavy metal bio- concentration in maize grains varies with time and type of metal.

At the first cropping season, BCF of boron in maize grains ranged from 0.222 in BA_{100} to 12.16 in BA_{100} + NPK₇₅. Among the sole BA treatments, the BA₅₀ treated plot had the highest BCF of boron. Generally, the sole NPK 20:10:10 treated plots were low in BCF of B compared with that of BA and PM. Blending BA with either PM or NPK increased the BCF of boron remarkably. In the second cropping season, there was a drastic reduction. For instance, in BA_{100} + NPK₇₅, the BCF of boron reduced by about 134% one year after application.

The BCF of cadmium was low at the first cropping season ranging from 0.009 in the control to 0.274 in the PM treated plots. However, at the second cropping season, the value increased remarkably in all plots ranging from 3.665 in $BA_{50} + NPK_{150}$ to 11.365 in NPK_{300} . The bio concentration factor of zinc was higher at the first cropping season and the least value (0.456) was obtained from the $BA_{50} + NPK_{150}$ plots, while, the highest (5.476) was observed in the control. At the second cropping season, the value reduced remarkably with the highest and lowest values obtained in maize grains harvested from plots treated with NPK₁₅₀ and $BA_{100} + Pm_5$ respectively.

The result revealed large differences in BCF depending on the type of amendment, time of cropping and on the metal in question. The bioavailability of B and Zn became less with time may be because of permanent immobilization by soil or biosolids reducing the

	В	oron	Cadmiu	ım	Zinc	
Treatment	1 st C. S	2 nd C. S	1 st C. S	2 nd C.S	1 st C.S	2 nd C.S
BA ₁₀₀	0.223	0.605	0.124	4.898	0.963	0.366
BA ₅₀	7.893	0.161	0.120	3.924	0.664	0.330
BA ₁₀	2.03	0.585	0.139	5.445	1.750	0.415
PM ₂₀	9.731	0.122	0.153	5.436	1.375	0.535
PM ₁₀	5.0	0.226	0.072	6.282	3.621	0.402
PM ₅	7.941	0.171	0.274	6.964	3.111	0.186
NPK ₃₀₀	1.607	0.712	0.132	11.365	2.842	0.438
NPK ₁₅₀	2.289	0.362	0.131	5.952	3.882	0.184
NPK ₇₅	2.417	0.364	0.135	7.857	2.359	0.412
$BA_{100} + PM_5$	3.445	0.217	0.165	6.958	0.902	0.797
$BA_{50} + PM^{10}$	11.068	0.098	0.189	4.814	0.663	0.403
$BA_{10} + PM_{20}$	11.11	0.096	0.148	8.274	1.381	0.365
$BA_{100} + NPK_{75}$	12.161	0.092	0.149	6.603	0.571	0.258
$BA_{50} + NPK_{150}$	9.941	0.188	0.140	4.863	0.456	0.407
$BA_{10} + NPK_{300}$	4.907	0.121	0.178	3.665	2.346	0.491
No amendment	3.519	0.171	0.009	5.845	5.476	0.370
Sd	3.970	0.200	0.0551	1.887	1.450	0.143

Table 44: Bio-concentration factor (BCF) of heavy metals in maize grains as affected by different rates of boiler ash, poultry droppings, NPK 20:10:10 and their combinations.

1st C.S= first cropping season , 2nd C.S= second cropping season, Sd=Standard deviation

chance of delayed õtime bomb effectö. However, there is concern that at the cessation of application, Cd bound metal would be released to soluble forms thus increasing the chance of delayed õtime bomb effectö.

In this study, the soil organic carbon and CEC showed positive correlation with Cd but negative with B and Zn. The result is in agreement with that of Bose and Bhattacharyya (2008) using wheat as a test crop. The result indicates that growing maize in soils amended with BA blended with either PM or NPK would represent a higher risk of food contamination than growing maize in sole BA, PM or NPK treated plots. However, applying either NPK or PM to boiler ash contaminated soils and growing maize in it, could be used for phyto remediation of lightly BA contaminated soils providing that the crop residues were safely disposed.

It is apparent from the present study that the maize plant absorbs heavy metals in different concentrations with respect to different amendments. Combined application of BA especially with NPK poses a threat of heavy metal accumulation in grains. The finding collaborate the assertion of Carbonell *et al.* (2011) that indiscriminate use of biosolids to improve agricultural yields without caring about any possible negative effects may be a major concern; thus the management of agricultural soils amendments must also consider plants nutritional needs and metal content for assessing the real potential toxicity and their risk for soils.

4.9. Correlation of Soil Properties with Maize Yield Parameters

4.9.1. Soil Physical Properties and Maize Biomass and Grain Yields

Table 45 shows the correlation coefficient matrix between soil physical properties; and maize biomass and grain yields. Silt content had significant (P<0.05) negative correlation with biomass yield at 8 and 12 weeks after planting (WAP)and grain yield implying its efficacy in detecting the biomass and grain yield of maize in the study area. Clay content positively correlated with grain yield while total and capillary porosity significantly correlated with biomass yield at 12 WAP. The result also revealed a significantly positive correlation between total and capillary porosity, available water capacity and biomass weight at 12 WAP.

The negative correlation between silt content and yield and of positive correlation between clay and grain yield indicates that increasing silt- sized fractions of the soil reduce

	BW(4WAP)	BW(8WAP)	BW(12WAP)	Grain Yield
C.Sand	-0.091	-0.284*	-0.188	-0.112
F.Sand	-0.155	0.297**	0.250*	0.049
Silt	0.012	-0.317**	-0.164	-0.364***
Clay	-0.092	0.146	0.001	0.347**
B.D.	-0.004	0.017	0.012	0.052
T.P.	0.134	0.080	0.253*	-0.113
C.P.	0.136	0.117	0.368***	-0.023
A.P.	0.062	0.090	0.115	-0.077
% A.S	0.083	-0.057	-0.094	0.126
%S.A.	0.032	-0.062	-0.066	0.091
MWD	0.041	-0.075	-0.49	-0.039
SHC	0.140	0.105	0.173	0.057
WHC	0.100	0,038	0.243	-0.156
WHC(60cm)	0.118	0.065	0.296*	-0.037

 Table 45: Correlation coefficient matrix between soil physical properties; and maize biomass and grain yields

BW=Biomass Weight S.H.C= Saturated Hydraulic Conductivity, % S. A =%state of aggregation, % A.S. =%Aggregate. Stability, MWD=Mean weight Diameter, W.H.C. =Water Holding Capacity, T.P. = Total porosity A.P. = Air porosity C.P. = Capillary porosity, B.D. = Bulk density*Significant at 0.05 level, ** Significant at 0.01 level ,*** Significant at 0.001 level

yield while increasing clay content increase yield. This may have influenced the low yield of the plots amended with 100 tha⁻¹ high silt-sized boiler ash. The significant positive correlation between available water capacity (WHC₆₀) and biomass yield at 12 WAP indicates that the amendments influenced the WHC₆₀ which impacted on the biomass yield.

4.9.2. Soil Chemical Properties and Maize Biomass and Grain Yields

Biomass yield at 4WAP was positively and significantly (p<0.05) correlated with soil sulphur content (r=0.254*). It was negatively and significantly correlated with exchangeable H⁺ (r=-0.399*).At 8WAP, biomass yield positively and significantly correlated with % N,P,K, Na, Ca²⁺,S, %BS and EC (Table 46).The soil heavy metal contents had negative and significant correlations with the biomass yield at this stage. At 12WAP, % C, Cu and Zn had significant correlation with the biomass yield.

The maize grain yield was positively and significantly (p<0.05) correlated with Na, Mn and B. It is however, negatively and significantly (p<0.05) correlated with % C, C.E.C and Zn. The positive and significant correlation between grain yield and boron and its non-significant relationship with Cd and Cu indicate the non-inhibitory effect of the usage of this boiler ash as soil amendment.

	Biomass (4WAP)	Biomass (8WAP)	Biomass (12WAP)	Grain yield
pH (H ₂ o)	0.138	0.175	0.339**	-0.162
%C	0.123	-0.342**	-0.166	-0.342**
%N	0.096	0.288*	0.410**	-0.123
Р	0.125	0.265*	0.411**	-0.124
K	-0.058	0.433***	0.435***	0.058
Na	0.008	0.541***	0.493***	0.274*
Ca ²⁺	0.020	0.478***	0.339**	0.159
Mg^{2+}	0.099	0.197	0.383**	-0.180
S	0.254*	0.279*	0.240	-0.049
%BS	0.057	0.527***	0.554***	0.088
C.E.C	-0.036	-0.307*	-0.087	-0.336**
EC	-0.116	0.543***	0.377**	0.141
Ex.Al ³⁺	-0.176*	0.083	-0.012	0.068
$\mathrm{Ex.H}^{+}$	-0.399*	-0.055	-0.103	-0.214
Mn^{4+}	-0.049	-0.097	0.146	0.322*
Во	-0.050	-0.418**	-0.366**	0.293*
Cd	0.151	-0.349**	-0.223	-0.243
Cu	0.145	-0.341**	-0.308*	-0.104
Zn	-0.116	-0.377**	-0.116	-0.277*

 Table 46: Correlation coefficient between maize biomass yield, grain yield and soil chemical properties

*Significant at 0.05 level, ** Significant at 0.01 level, *** Significant at 0.001 level

4.9.3. Soil Physical Properties and Nutrient and Heavy Metal Concentrations in Maize Grains.

Table 47 reveals the correlation coefficient of the soil physical properties and nutrient and heavy metal concentration in maize grains. The silt fraction of the soil correlated positively and significantly with the grain K and S while, it negatively and significantly correlated with grain- % N, Na, B and Zn. Boron concentration in the maize grain positively correlated with the clay particle size fractions, as Cd correlated positively with the MWD. Similar negative correlations of clay with Cd uptake by plants has been reported by Orhue *et al.* (2011) and Qrhue and Izunwanne (2013). The bulk density did not significantly correlate with any of the nutrients or metals measured.

The implication of positive correlation is that as the soil parameter increases, the maize grain concentration of the nutrient or heavy metal in question increases while the negative correlation indicates that as the soil parameter in question decreases the concentration of the nutrient/metal increases.

Maize grain									
	%N	%P	K	S	Na	Bo	Cd	Cu	Zn
C.sand	-0.083	-0.221	-0.210	0.070	-0.119	-0.341**	0.146	0.089	-0.083
F.sand	0.001	0.057	0.108	-0.035	0.076	0.273	-0.110	-0.153	0.047
Silt	-0.305*	0.112	0.348**	0.415**	-0.406**	-0.507***	0.485	-0.213	-0.363**
Clay	0.267*	0.151	0.313	-0.281*	0.288*	0.417**	-0.312***	0.215	0.232*
% A.S.	-0.233	0.128	-0.214	0.287	-0.284*	-0.219	0.226*	-0.267*	-0.311
% S.A.	-0.170	0.147	-0.173	0.207	-0.248*	-0.221	0.166	-0.216	-0.255
MWD	-0.242	0.001	-0.207	0.325	-0.338**	-0.304*	0.286*	-0.394*	-0.381**
B.D.	-0.118	-0.038	0.146	-0.027	0.111	0.116	-0.144	0.082	-0.108
S.H.C	0.251*	-0.025	0.165	-0.078	0.180	-0.125	-0.123	0.095	0.112
W.H.C.	0.092	0.041	-0.066	0.011	-0;012	-0.200	0.123	0.095	0.112
W.H.C.60cm	0.017	0.087	-0.157	0.075	-0.024	-0.197	0.202	-0.068	0.067
T.P	0.054	-0.040	0.075	-0.003	0.088	-0.038	0.001	0.085	0.053
C.P	-0.020	0.002	-0.043	0.018	0.098	-0.079	0.061	0.058	0.016
A.P.	0.191	-0.038	0.272*	-0.185*	0.141	0.080	-0.216	0.139	0.116

 Table 47: Correlation coefficient between grain concentrations of nutrients, heavy metals and soil physical properties

S.H.C= Saturated Hydraulic Conductivity, % S. A = % state of aggregation, % A.S. =%Aggregate. Stability, MWD=Mean weight Diameter, W.H.C. =Water Holding Capacity, W.H.C_{60cm}. =Water Holding Capacity at 60cm tension, T.P. = Total porosity A.P. = Air porosity C.P. = Capillary porosity, B.D. = Bulk density.

4.9.4. Soil Chemical Properties and Nutrient and Heavy Metal Concentration in Maize Grains.

Table 48 presents the correlation coefficient matrix between grain concentrations of nutrients and heavy metals, and soil chemical properties as influenced by the application of the amendments. Maize grain nitrogen content correlated strongly and negatively with soil % C (r= -0.619^{***}) and Bo (r= -0.728^{***}). Cadmium content of the grain was strongly and positively correlated with the soil Cd, % C and Na⁺ content.

	Grain								
	%N	Р	K	S	Na	Во	Cd	Cu	Zn
pH(H₂O)	0.16	-0.01	0.06	-0.02	0.16	0.07	0.06	0.22	0.18
% OC	-0.62***	0.07	-0.73***	0.63***	-0.67***	-0.56***	0.63***	-0.35**	-0.56***
% N	0.25*	-0.11	0.10	-0.16	0.24	0.08	-0.04	0.15	0.32*
Р	0.26*	0.015	0.08	-0.07	0.18	0.02	0.04	0.21	0.22
Κ	0.66***	0.053	0.64***	-0.63***	0.67***	0.51***	-0.53***	0.41**	0.60***
Na^+	0.76***	-0.11	0.80***	-0.76***	0.74***	0.59***	0.70***	0.49**	0.77***
Ca^{2+}	0.75***	-0.208	0.66***	-0.71***	0.65***	0.58***	-0.72***	0.42**	0.74***
Mg^{2+}	0.23	0.06	0.01	-0.04	0.15	0.04	0.15	0.20	0.16***
S	0.69***	0.09	-0.66***	0.73***	-0.71***	0.57***	0.66***	0.44***	-0.701***
% B.S	0.77***	-0.13	0.69***	-0.68***	0.72***	0.58***	-0.60***	0.51***	0.74**
C.E.C	-0.32**	0.03	-0.55***	0.33**	-0.35**	0.46***	0.50***	-0.17	-0.38**
EC	0.69***	-0.22	0.71***	-0.73***	0.76***	0.74***	-0.72***	0.42**	0.74**
Ex. Al ³⁺	0.21	0.29	0.46***	-0.28*	0.26*	0.56***	-0.37**	0.05	0.21
Ex. H^+	0.33**	-0.32	0.21	-0.40**	0.39**	0.24	-0.42**	0.22	0.40**
Mn^{4+}	0.09	-0.04	-0.13	0.02	-0.05	-0.18	0.08	-0.01	0.16
В	-0.73***	-0.04	-0.82***	0.70	-0.66***	-0.77***	0.65***	-0.55***	-0.73***
Cd	-0.66***	0.17	-0.81***	0.71	-0.75***	-0.72***	0.77***	-0.36**	-0.74***
Cu	-0.62***	0.08	-0.61***	0.73	-0.59***	-0.51***	0.70***	-0.32**	-0.70***
Zn	-0.12	0.12	-0.24	0.14	-0.25*	-0.23	0.37**	-0.08	-0.09

 Table 48: Correlation coefficient between grain concentrations of nutrients, heavy metals and soil chemical properties

%OC= percent organic carbon, % N =percent nitrogen, P = Phosphorus, K = Potassium, Na⁺ = Sodium, Ca²⁺ Calcium, Mg²⁺ = Magnesium, S = Sulphur, % BS = Percent Base Saturation, C, E.C. = Cation exchange capacity, EC= Electrical conductivity, Ex. Al³⁺ = Exchangeable Aluminum, Ex. H⁺ = Exchangeable Hydrogen, Mn = Manganese, B = Boron, Cd= Cadmium, Cu = Copper, Zn = Zinc. Correlation values are based on pooled data from the treatments in the first and second cropping seasons.* Significant at 0.05 level ** Significant at 0.001

4.9.5. Correlation Coefficient Matrix between Maize Growth and Yield Traits.

The result of the correlation analysis of the maize growth and yield traits is shown in Table 49. The r^2 =values ranged from -0.67 (correlation between plant height and days to 50% tasselling) to 0.90 (Correlation between grain yield and cob weight). Among the growth factors, leaf area index most correlated (=0.63***) with grain yield, followed by biomass weight (r^2 =0.61***). Days to 50% tasselling and silking were negatively but weakly correlated with grain yield. Plant height had the highest correlation with the biomass yield.

		v								
GY	*									
BMW	0.611	*								
Cob wt	0.904	0.733	*							
100 SW	0.515	0.505	0.478	*						
LAI	0.633	0.733	0.646	0.608	*					
LN	0.356	0.533	0.432	0.734	0.689	*				
PH	0.418	0.793	0.502	0.501	0.767	0.643	*			
SD	0.536	0.748	0.585	0.622	0.761	0.672	0.766	*		
DT	-0.326	-0.558	0.428	0.182	0.594	-0317	0.573	0.502	*	
D.S	-0.329	-0.629	0.438	0.370	0.640	0.489	0.670	0.585	0.873	*
	GY	BMW	Cob wt	100 -SW	LAI	LN	PH	SD	DT	D.S

Table 49: Correlation Values among the Growth and Yield Traits measured in this study

Correlation values are based, on pooled data from the treatments in the first and second cropping seasons. All the traits were significantly correlated with each other at p<0.00. Gy= grain yield, BMW= Biomass weight, Cob wt= cob weight, 100-sw= 100- grain weight, LAI= leaf area index, LN= leaf number, PH= plant height, S= stem diameter, DT= days to 50% tasselling, DS= days to 50% silking.

CHAPTER FIVE

SUMMARY AND CONCLUSION

This study compared the agronomic potentials of boiler ashes (BA) generated from combustion of oil palm mill wastes at Solive Vegetable Mills Ltd, Nsukka with that of poultry droppings (PM) and mineral fertilizer (NPK 20-10-10). The physical and chemical properties of the boiler ash were obtained using appropriate physico-chemical techniques. The effect of the ash, PM, and NPK 20-10-10 as well as their combinations, were evaluated for two consecutive years in the field using maize (*Zea mays*) as the test crop. The main objective was to compared the crop-use potentials of BA with that of poultry droppings (PM), inorganic fertilizer and their combinations as well as their effects on an Ultisol and maize performance.

The result of the physical properties of the ash showed that it had predominately sandsized particles, low bulk density and high moisture content. Chemically, it is alkaline in nature and rich in essential plant nutrients except nitrogen and also relatively low in toxic heavy metal concentration when compared to PM and NPK mineral fertilizer. Potentially, it is richer in phosphorus than PM.

Application of high rate of boiler ash significantly altered the mechanical composition of the soil by increasing the silt- sized particles. Soil bulk density and aggregate stability were reduced; porosity and water holding capacity increased but saturated hydraulic conductivity remained unchanged. This implies that application of high rate of boiler ash increases the chances of plant survival under extended water stress in soils. The high sodium content of the ash could not exert significant influence to alter the saturated hydraulic conductivity. Application of boiler ash at 50tha⁻¹ reduced aggregate stability to water by only 4% relative to the control.

There was a significant increase in the pH of the soil following the application of the amendments although; it did not exceed 7.7 in any treatment. Average soil pH was increased from 1.3 to 2.5 units compared to the control after boiler ash application of 10-to100 tha-¹. Blending NPK fertilizer with low rates of boiler ash obliterated the acidic effect of NPK fertilizer.

Sole application of high level of boiler ash (100 tha⁻¹) significantly increased soil N by 47 and 39% at the first soil application and residual cropping respectively. Generally, BA_{100} + PM_5 amended plots had the highest soil total N at both cases. Percent organic carbon was higher under residual effects of integrated treatment involving boiler ash and NPK fertilizer. The highest available P content was recorded in plots amended with BA_{50} + NPK_{75} , and BA_{100} +

 PM_5 at the first soil application and residual cropping seasons respectively. The lowest application rate of boiler ash (10tha⁻¹) increased available P higher than the highest rate of poultry droppings or NPK 20:10:10. The $BA_{10} + PM_{20}$ amended plots had the highest sulphur content while higher Mg content and C.E.C were recorded in $BA_{100} + NPK_{75}$.

High levels of NPK fertilizer induced the highest increase in boron but amending it with BA₁₀ obliterated it and reduced it further. However, boron toxicity was not of any concern in this study. Maximum zinc concentration was found in BA₁₀₀. Boiler ash application significantly reduced mobile aluminum from 1.5mgkg⁻¹ in the control soil to non-detectable levels at both seasons. Hydrolytic acidity was, however, increased.

Preliminary agronomic evaluation-using maize as a test crop showed that high rate of boiler ash (100tha⁻¹) reduced percentage maize germination but residual effect increased the germination percentage. The development of the maize crop was severely hindered by the application of boiler ash at the rate of 100tha⁻¹ at the first cropping season. The tallest plants were obtained in plots amended with $BA_{10} + PM_{20}$, which incidentally had the widest stem diameter. Highest number of leaves was obtained from plants grown in $BA_{50} + PM_{10}$ treated plots. The highest leaf area index (7.32) was obtained in $BA_{10} + PM_{20}$ and $BA_{50} + PM_{10}$ treated plots at the first and second cropping seasons respectively. Maize biomass yield at 12 WAP was highest in plots amended with $BA_{50} + PM_{10}$ and $BA_{10} + PM_{20}$ at the first and second cropping seasons respectively. The result of the maize growth rate evaluation indicated that application of boiler ash up to 50tha⁻¹ increased maize growth rate but reduced when applied at 100tha⁻¹.

Maize plants grown in plots treated with $BA_{10} + PM_{20}$ recorded the highest grain yield at the first soil application and at the residual cropping seasons. Among the sole boiler ash treated plots, BA_{10} had the highest grain yield at both cropping seasons. The highest 100-grain weight was obtained in the $BA_{10} + PM_{20}$ treated plots. Comparatively, plots treated with poultry droppings gave higher yield than NPK fertilizer treated plots.Generally,maize grain yield was lower at the second cropping season. The results of the first cropping season indicate that BA_{50} + NPK $_{150}$ had the least harvest index, while the highest was in PM_{20} treated plots. The sustainable yield index was greater in all the plots under poultry droppings treatment and lower values were recorded at the second cropping season.

Maize grain nutrient concentration was significantly influenced by the different treatments. Highest grain nitrogen and zinc content was observed in plots treated with BA_{100} at both cropping seasons while available P did not differ significantly at the first cropping season. Residual effect of PM_5 had the highest maize grain available P content. Highest grain K content was obtained in BA_{10} + NPK₃₀₀ treated plots while highest grain sulphur was obtained from

 $BA_{10} + Pm_{20}$. Boron concentration was highest in maize grains harvested from plots treated with $BA_{100} + NPK_{75}$, while cadmium accumulation in grain should be of concern. The following conclusions were drawn from the study:

- 1. Oil palm based industrial boiler ash is dominated by sand-sized particles, has low bulk density (BD), high water holding capacity (WHC), favourable pH and contains high proportion of essential plant nutrients especially P, K; non toxic levels of micronutrients but low N content, thus its agronomic potentials are fairly comparable to PM and NPK.
- 2. Integration of low rate (10tha⁻¹) of BA with poultry droppings rather than costly inorganic fertilizers like NPK 20-10-10 has the potential to serve as organic fertilizer for sustaining high crop yield but to improve soil physical properties such as bulk density, porosity, aggregate stability and water holding capacity require application rates of \times 50 tha⁻¹.
- Boiler ash addition in the soil resulted to an apparent change in texture, and particle size ó distribution levels, lower bulk density, higher water holding capacity, increased soil OC, N, exchangeable K, Ca, Mg and Mn as well as reduced hydrolytic acidity.
- 4. Application of boiler ash at the rate of 100 tha⁻¹ has the potential to impede germination, growth and yield of maize on the short run, while utilization of $BA_{50} + PM_{10}$ proved a better alternative to conventional recommended NPK fertilizer in increasing nutrient availability and maize performance in an Ultisol.
- 5. Concentrations of N, P, K and Zn were found to be greater in maize grains harvested from sole boiler ash amended plots with non- toxic levels of B, Cd, and Zn. Therefore, its use as soil conditioner is safe health-wise.

Further Studies

Oil palm boiler ash is a new industrial waste and needs to be studied further. The following is a list of recommendations for future boiler ash studies.

- 1. Evaluate the effect of boiler ash application on other cereals, vegetables and forage crops and other soil types.
- 2. Evaluate the effect of time and method of application and cumulative residual effects on soil properties and crop productivity.
- 3. Evaluate soil physico- chemical and biological responses to boiler ashes under different cropping systems on various soils.
- 4. Evaluate the effects of boiler ash on survival and activities of soil pathogenic organisms.
- 5. Study the use of boiler ash in combination with other residuals in restoring metalcontaminated mining areas and oil polluted sites.
- 6. Evaluate the bio-geochemical cycling of nutrients in boiler ash amended soils.
- 7. Study the potentials of boiler ash in integrated plant nutrient management system.

REFERENCES

- Abdulraheem, M.I.,Ojeniyi, S.O., and Charles, E.F., 2012. Integrated application of urea and sawdust ash: effect on soil chemical properties, plant nutrients and Sorghum performance. Agric. and Vet. Sci. 1 (4):38-41.
- Abedi, T., Abernzadeh, A., and Kazemeini, S.A., 2010. Effect of organic and inorganic fertilizers on grain yield and protein banding pattern of wheat. Australian Jour. of Crop Sci. 4 (6): 384-389.
- Abernethy, R.F., Peterson, M.J., and Gibson, F.H., 1969. Major ash constituents in U.S. coals, Report of investigation 7240, Bureau of mines.
- American Coal Ash Association (ACAA), 1999. 1998 coal combustion product (CCP)production and use (short Tons). American coal Ash Association, Alexandria, VA.
- Adejobi, K. B., Famaye, A.O., Oloyede, A.A., Oyedokun, A.V., Adesoun, S.A., and Adenyi, D.O., 2011. Effects of organo-mineral fertilizer and cocoa pod husk ash on the soil leaf chemical composition and growth of Coffee. Niger. Jour. of Soil Sci. 21 (2): 45 51.
- Adekiya, A.O., Ojeniyi, S.O., and Agbede, T.M., 2012. Poultry droppings effects on soil properties leaf nutrient status, growth and yield of cocoyam in tropical alfisol. Nig.Jour.Soil Sc. 22(2): 30-39.
- Adeleye, E.O., Ayeni, L.S., and Ojeniyi, S.O., 2010. Effect of poultry droppings on soil physico-chemical properties, leaf nutrient contents and yield of yam (*Dioscorea rotundata*) on alfisol in southwestern Nigeria. Journal of American Sci. 6 (10): 871-878.
- Adeoye, K.B., 1986. Physical change induced by rainfall in the surface layer of an Alfisol, Northern Nigeria. Geoderma. 39:59-66.
- Adesodun, J.K., Mbagwu, J.S.C. and Oti, N., 2005. Distribution of carbon, nitrogen and phosphorus in water stable aggregates on an organic waste amended Ultisol in Southern Nigeria. Bio Resource Tech. 96:509-56.
- Adjei-Nsiah, S., 2012. Response of maize (Zea mays L.) to different rates of palm bunch ash application in the semi-deciduous forest agro-ecological zone of Ghana. Applied and Environ. Soil Sci. 2012.
- Adjei-Nsiah, S. and Obeng, C.B., 2013. Effect of palm bunch ash application on soil and plant nutrient composition and growth and yield of garden eggs, pepper and okra. International Jour. of Plant and Soil Sci. 2(1): 1-15.
- Adriano, D.C., Page, A.I., Elseewi, A.A., Chang, A.C. and Staughan, I., 1980. Utilization and disposal of fly ash and other coal residues in terrestrial ecosystem: a review. Jour of Environ. Qual. 9:333-344.

- Agba, O.A., Ubi, B.E., Abam, P., Ogbechi, J., Akeh, M., Odey, S., and Ogar, N., 2012. Evaluation of agronomic performance of maize (Zea mays L.) under different rates of poultry droppings application in an ultisol of Obubra, Cross River State, Nigeria. Int. Jour. Agric. and For., 2 (4): 138 144.
- Agbede, T. M., and Adekiya, A.O., 2012. Effect of wood ash, poultry droppings and NPK fertilizer on soil and leaf nutrient composition, growth and yield of okra (Abelmoschus esculentus). Emir. J. Food Agric. 24 (4) 314-321.
- Agbede, T.M., Ojeniyi, S.O., and Adeyemo, A.J., 2008. Effect of poultry droppings on soil physical and chemical properties, growth and grain yield of sorghum in southwest, Nigeria. Am-Eurasian J. Sustain. Agric., 2 (1): 72-77.
- Aggarwal, S., Singh, G.R., and Yadav, B.R., 2009. Utilization of fly ash for crop production, effect on the growth of wheat and sorghum crops and soil properties. Jour. Agrophys.9: 20-23.
- Agusalim, M., Wani, H.U., and Syechfani, M.S., 2010. Rice husk biochar for rice based cropping system in acid soil. The characteristics of rice husk biochar and its influence on the properties of acid sulfate soils and rice growth in west Kalimantan. Indonesia Jour.Agric. Sci. 2(1): 39-47.
- Ahnstrom, Z. S., and Parker, D. R., 1999. Development and assessment of a sequential extraction procedure for the fractionation of soil cadmium. Soil Sci. Soc. Am. Jour. 63:1650-1658.
- Ahmad, N., Hassan, F. AND Qadir ,G. 2007. Effect of subsurface soil compaction and improvement measures on soil properties. International Journal of Agriculture & Biology ,96365096513
- Aigbodion, V.S., Hassan, S.B., Ause, T., and Nylor, G.B., 2010. Potential ultilization of solid waste (Bagasse ash). Jour. Mineral & Mat. Character and Eng.9 (i) 67-77
- Aitken, R.L., 1992. Relationships between extractable Al, selected soil properties, pH buffer capacity and lime requirement in some acidic Queensland soils. Aust. J. Soil Res. 30, 1196130.
- Aitken, R.L., and Bell, L.C., 1985. Plant uptake and phytotoxicity of boron in Australian fly ashes. Plant & Soils. 84:245-257.
- Aitken, R.L., Campbell, D.J., and Bell, L. C., 1984. Properties of Australian fly ashes relevant to their agronomic utilization. Aust. Jour. Soil Res. 22:443-453.

- Akamigbo, F.O.R., and Igwe, C.A., 1990. Morphology, Geography, genesis and taxonomy of three soils series in Eastern Nigeria. Samaru Jour. Agric. Res. 7:33 48.
- Akinmutimi, A.L., 2014. Effects of cocoa pod husk ash and NPK fertilizer on soil nutrient status and sweet potato yield in an Ultisol in Southern Nigeria. Int. Jour. of Advanced Res. 2 (2):814-819.
- Alamgir, M., McDonald, C.H., Roehl, K.E., and Ahsan, A., 2005. Integrated management and safe disposal of municipal solid waste in least developed Asian countries. A feasibility study. p 83. Khulna University of Engineering and Technology, Khulna, Bangladesh.
- Allison, L.E., 1982. Organic Carbon. In: Method of Soil Analysis. Part 2 Black, C.A et al.. (ed) Am. Soc. Agron.9:1368 1398.
- Al-Moaikal, R. M. S., 2006. Physiological effects of gibberellic acid and polyamine(s) on germination and seedling growth of *Zeamays* stressed with sodium chloride salinity. Ph.D. Thesis, Botany Dept., Science College for girls, dammam.
- Alva, A.K., 1994. Possible utilization of fuel and desulphurization gypsum and fly ash for citrus production: Evaluation of crop growth response. Waste management, 14 (7): 621-627.
- Amanullah, J., Ali, S., Ahmad, T., and Ahmad, I., 2014. Impact of soil amendments on yield and yield attributes of maize (Zea mays) under different irrigation schedule. J. Environ and Earth Sci. 22(4): 132-140.
- Amiralian, S., Amin C., and Hamid N., 2012. Investigation on the effect of lime and fly ash on hydraulic conductivity of soil. Inter. Jour. of Biology, Ecology and Environ.Sci.,1 (3): 120-123.
- Amusan, O.A., and Ojeniyi, S.O., 2011. Effect of integrated application of soil amendments on nutrient uptake and soil properties in a tropical Alfisol. Nigerian Jour. Soil Sci., 2 (2) 24 34.
- An, Y.J., 2006. Assessement of comparative toxicities of lead and copper using plant assay.ö Chemosphere 62 (8): 1359-1365
- Anderson, D.A., 1978. õ Utilization of bottom ash in highway constructionö Proceedings International Conference on the use of by-products and waste in civil Engineering Vol.2, Paris, France, November 28-30.pp.322-332.
- Ano, A.O., and Agwu, J.A., 2005. Effect of animal manure on selected soil chemical properties, organic matter, pH,exchangeable Ca, and Mg. Nigerian Jour. of Soil Sci. 15(1): 14 19.

- Ano, A.O., and Ubochi, C.I., 2007. Neutralization of soil acidity by animal manures: mechanism of reaction. African Journal of Biotechnology 6(4):364-368.
- Ansari, F. A., Gupta, A.K., and Yunus, M., 2011. Fly ash from coal-fed thermal power plants: Bulk utilization in Horticulture- A long- term risk management option. Int. Jour. Environ. Res. 5(1):101 108.
- Aronsson, K.A., and Ekelund, N.G.A., 2004. Biological effects of wood ash application to forests of wood ash application to forest and aquatic Ecosystem. J. Environ. Qual. 33:1595 1605.
- Arshad, M., Khalid, A., Mahmood, M.H., and Zahir, Z.A., 2004. Potential of nitrogen and Ltryptophan enriched compost for improving growth and yield of hybrid maize. Pak., Jour. Agric. Sci., 41: 16 24.
- Arvidsson, H., and Lundkvist, S., 2003. Using pulverized fuel ash Victorian Brown coal as a source of nutrients for pasture species. Austr. Jour. of Expt. Agric. Animal Husbandry, 20:377 384.
- Asadu, C.L.A., 1990. A comparative characterization of two foot-slope soils in Nsukka area of Eastern Nigeria. Soil Science 150:527-534. USA
- Assouline, S., 2004. Rainfall-induced soil sealing. A critical review of observation, conceptual models and solutions. Vadose Zone. Jour.3:570-591.
- Ausari, F.A., Gupta, A.K., and Yunus. M., 2011. Fly ash from coal-fed thermal power plants: Bulk utilization in Horticulture-A long term risk management option. Int. Jour. Environ. Res. 5 (1): 101-108.
- Ayeni, L.S., 2008. Integrated Application of Cocoa Pod Ash And NPK Fertilizer on Soil Chemical Properties and Yield of Tomato. American óEurasian Journal of sustainable Agriculture. 2 (3):333 ó 33.
- Ayeni, L.S., and Adeleye, E.O., 2009. Comparative effect of integrated application of cocoa pod ash, poultry manure and NPK fertilizer on soil Nitrogen, organic carbon and phosphorus contents ó incubation study. Soil Nature 3 (2): 15- 19.
- Ayeni, L.S., Adetunji, M.T., Ojeniyi, S.O., Ewulo B.S., and Adeyemo, A.J., 2008. Comparative and cumulative effect of cocoa pod husk ash and poultry droppings on soil and maize nutrient contents and yield. American -Eurasian Jour. Sustainable Agric. 2 (1) 92-97.

- Ayiniuola, G.M., and Olaosebikan, O.1., 2013. Influence of rice husk ash on soil permeability. Transnational Jour. of Sci. and Tech.3 (10): 29-33.
- Ayuso, E.A., Querol, X., and Tomas, A., 2006. Environmental impact of a coal combustion desulphurization plant Abetment capacity of desulphurization process and environmental characterization of combustion products.ö Chemosphere 65: 2009-2017
- Aziz, S.A. and Karim, S.M.,2016. The effect of some soil physical and chemical Properties on soil aggregate stability in different locations in Sulaimani and Halabja Governorate. Open Journal of Soil Science, 6, 81-88.
- Bath, E., Frostegard, A., Pennanen, T., and Fritize, H., 1995. Microbial community structure and pH response in relation to soil organic matter quality in wood-ash fertilized clear-cut or burned coniferous forest soils. Soil Biol. Biochem., 27:229-240.
- Babadele, D.O., and Ojeniyi, S. O., 2013. Nutrient concentration and root count of cassava as influenced by residue and NPK fertilizer. Niger. Jour. of Soil Sci. 23 (2): 276-281.
- Barry, G.A., Gardner, E.A., Rayment, G.E., and Bloesch, P.M., 1999. Recycling organic materials on agricultural lands. 1999 RO conference papers.
- Basu, M., Pande, M., Bhadoria, P.B.S., and Mahapatra, S. C., 2009. Potential fly-ash utilization in Agriculture: A global review: Progress in Natural Sci., 19:1173-1186.
- Bertschi, A.B., 2000. The growth response of Assiniboine popular and Harrington barley to wood ash additions. M.Sc. Thesis. University of Alberta, Department of Renewable Resources.
- Bhattacharya, R., Kundu, S., Prakash, V., and Gupta, H.S., 2008. Sustainability under combined application of mineral and organic fertilizers in a rain-fed soy bean-wheat system of Indian Himalayas. Euro. Jour. Agron. 28:33 46.
- Blake, G.R., and Hartge, K.H., 1986. Bulk density. In: Klute, A. (Ed). Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods ASA N0.9, Madison, Wisconsin U.S.A.
- Boh, M.Y., Muller, T.,and Saverborn, J., 2013. Maize (Zea mays L.) response to urine and wood ash fertilization under saline (Nacl) soil conditions. Inter. Jour. of Agric. Science 3 (4): 333-345.
- Borm, P, 1997. Toxicity and occupational health hazards of coal fly ash(CFA). A review of data and comparison to coal mine dust. Ann. Occup. Hyg.1977 Dec,41(6):659-76.

- Bose, S., and Bhattacharyya, A.K., 2008.Heavy metal accumulation in wheat plant grown in soil amended with industrial sludge. Chemosphere 70: 126461272.
- Brady, N.C., and Weil, R.R. 1999. The Nature and Properties of Soil. 12th Ed. Prentice-Hall,Inc., Upper Saddle River, NJ. p881.
- Brady, N.C., and Weil, R.R., 2005. The nature and properties of soil,14th Ed. Prentice-Hall,Inc., Upper Saddle River, NJ. p881.
- Brasil, 2007. Ministério da Agricultura, Pecuária e Abastecimento. Instrução Normativa nº 17, de 21 de maio de 2007. Aprovaos Métodos Analíticos Oficiais para Análise de Substratose Condicionadores de Solos, na forma do Anexo à presente Instrução Normativa. Diário Oficial da União da República Federativa do Brasil, Brasília, 24 de maio de 2007.
- Bray R.N., Kurtz, L.T., 1945. Determination of total organic and available forms of phosphorus . Soil Sci, 59: 39645.
- Bremner, J.M., 1996. Total nitrogen. In, Page et al. (eds) Methods of Soil Analysis, part 3 Chemical methods. Soil Sci. Soc. America Book Ser. 5.
- Brod, E.M., 2011.Combined waste resources as NPK fertilizer: results from a pot experiment. Master degree Thesis in Agroecology, Department of landand environmental Sciences. Norwegian University of life science.
- Brown, S.L., Henry, C.L., Chaney, R., Compton, H., and De Volder, P.S., 2003. Using municipal bio-solids in combination with other residuals to restore metal-contaminated mining areas. Plant and Soil, 249: 203-215.
- Brown, T.H., Bland, A. E., and Wheeldon ,J.M .,1997. Pressurized fluidized bed combustion ash 2. Soil and mine spoil amendment use options. Fuel, 76 (8), 741-748.
- Bruand, A., Hartmann, C., and Lesturge, G.,2005. Physical properties of tropical sandy soils. A large range of behaviours. www.fao.org./docrep/010.
- Buck, J.K., Honston R.J., and Beimboron, W.A., 1990. Direct seedling of anthracite refuge using coal fly ash as a major amendment. In:Proceeding of the mining and reclamation conference and exhibition .West Virginia Univ. Pub. Service No.2. p.603.
- Buddhe, S.T., Thakre, M., and Chaudhari, P.R., 2014. Effect of fly ash based soil conditioner (Biosil) and recommended dose of fertilizer on soil properties, growth and yield of wheat. American J. of Engineer. Res. 3 (1): 185-199.
- Campbell, A.G., 1990. Recycling and disposing of wood ash. Tappi J.73:141 146

- Capriel, P., Beck, T., Borchert, H., and Harter, P., 1990. Relationship between soil aliphatic fractions extracted with super critical hexane: soil microbial biomass and soil aggregate stability. Soil Sci. Soc. Am. Jour. 54:415-420.
- Carbonell, G., Miralles de imperial, R., Torryos, M., Delgado, M., and Rodriguez, J.A., 2011. Effects of municipal solid waste compost and mineral fertilizer amendments on soil properties and heavy metal distribution in Maize plants (Zea mays L.). Chemosphere, 85:1614–1623.
- Carlile, C., Nadigaer, S., and Burken, J.,2013. Effect of fly ash on growth of mustard and corn. Bio. Sci., Biotech. Res. Asia, 10 (2): 551-557.
- Carlson, C.L, Adriano, D.C, Sajwan, K.S., Abels, S.L., Thomas, D.P., and Driver, J.F., 1991. Effect of selected trace metals on germinating seeds of six plant species. Water, Air and soil pollution 59, 231-240.
- Catricalla, C.E., Bowden, W.B., Smith, C.T., and MC-Dowell, H., 1996. Chemical characteristics of leachate from pulp and paper mill residuals used to reclaim a sand soil. Water Air and Soil Pollution. 89:171 192.
- CFRI (Central Fuel Research Institute),2003. Bio-restoration of O.B. Dumps through the plantation of selected efficient photosynthetic/soil conserver species in Eastern Jharia coal fields (Sponsored by SSRC Dept. of coalö CFRI, Dhan bad, Jharkhard CFRI Report No. TR/CFRI/101/2002-2003.
- Cha, D.W, Lee H.S., and Jung, J.H., 1999. Production and composition of power plant coal in Korea. In. Proc. Agricultural utilization of fly ash symposia Gyenogsang National University. July 1-23.
- Chaney, R. L., 1993. Zinc phytotoxicity. *In* Zinc in Soils and Plants. Eds. A D Robson. Kluwer Academic, Dordrecht, The Netherlands.
- Chang, A.C., Lund, L.J., Page, A.L., and Warneke, J.E., 1977. Physical properties of fly ash amended soils. J. Environ. Qual. 6:267-270.
- Chang, M.B., and Ku, S. R., 1998. Fates and partitioning of heavy metals in municipal solid waste incineration process. Toxicol. Environ.Chem.67:161-169.
- Chirenje, T., and Ma, L.O.,1999. Effects of acidification on metal mobility in a paper mill- ash amended soils. Jour. Environ. Qual.28:760-766.
- Chirenje, T., and Ma, L.Q., 2002. Impact of high volume wood-fired boiler ash amendment on soil properties and nutrients. Commun. Soil Sci. Plant Analy.33 (1&2),1 -17.

- Danalatos, N.G., Kosmas, C.S., Driessen, P.M., and Yassoglou, N., 1994. Estimation of the draining soil moisture characteristics from standard data as recorded in soil surveys. Geoderma 64: 155-165.
- Daniel, L., Stewart, B., Haering, K., and Zipper, C., 2002. The potential for beneficial re-use of coal fly ash in southwest Virginia mining environments. Virginia cooperative Extension. Pub. 460-134.
- Das, B.K., Choudhury, B.H., and Das, K.N., 2013. Effect of integration of fly ash with fertilizers and FYM on nutrient availability, yield and nutrient uptake of rice in Inceptisols of Assam. India. Int. Jour. Advancements in Res & Tech. 2 (11): 190-208.
- Davison, R.I., Natusch, D.F.S., Wallace, J.R., and Evans, C.A Jr. ,1974. Trace elements in fly ash: dependence of concentration on particle size. Environ Sc. Technol.8:1107-1113.
- De Bano, L.F., 1969. Observations on water-repellent soils in western United States. In: DeBano, L.F., Letey, J. (Eds.),Proceedings of a Symposium on Water Repellent Soils. University of California, Riverside, 6610 May 1968. pp. 17629.
- Demeyer, A., Nkana, J.C.V., and Verloo M.G., 2001. Characteristics of wood ash and influence on soil properties and nutrient uptake: an Overview. Bioresour. Technol. 177:287-295.
- Demirbas, F., Balat, M., and Balat, H., 2009. Potential contribution of biomass to sustainable energy development. Energy Convers. Manag., 50, 174661760.
- Diebel, J., Mc-Ginnis, G., Pughani, T., Shetron, S., and Jurgensen, M., 1992. The environmental fate of wood ash applied to soils. In : Proc. Waste wood processing and combustion for energy. 5th Annual National Biofuels Conf. Boston, M.A. P. 359-368.
- Egloffstein, T.A., 2001. Natural bentonitesóinfluence of the ion exchange capacity and partial desiccation on permeability and selfóhealing capacity of bentonites used in GCLs. Geotextiles and Geomembranes, 19: 4276 444.
- Eichler-Löbermann, B., Schiemenz, K., and Makadi, M., 2008. Nutrient cycling by using residues of bioenergy production, II: Effects of biomass ashes on plant and soil parameters. Cereal Res. Commun. 36:125961262
- Eisenberg, S.H., Tittlebaun, M.E., Easton, H.C., and Soroczal, M.M., 1986. Chemical characteristics of selected fly ash leachates.Jour. Environ. Sci. Health, 21:383-402.
- Enrich, M.S., and Ohno, T., 1992. Phosphorous availability to corn from wood ash-amend soils. Water, Air, Soil Pollu.64:475-485.
- Enwezor, W.O., Udo, E.J., Usoroh, N.J., Ayotade, K.A., Adepetu, J.A., Chude, V.O. and UdegbeC.I., 1989. Fertilizer use and management for crops in Nigeria. FPPD, Federal

Ministry of Agriculture, Water Resources and Rural Development, Lagos, Nigeria. Pp.163.

- EPA, 2007. The use of soil amendment for remediation, revitalization and reuse. Solid waste and Emergency response (5203p).www.epa.gov
- Ermson, Z.N., David, A.M., Thomas, R.W., Dexter, B.W., Henry, A.T., and Douglas R.S., 2011. Tillage and fertilizer management effects on soil atmospheric exchanges of methane and nitrous oxide in corn production system. Applied and Environmental Soil Sci. 10:1155/2011/475.
- Esuden, J.D., Eigbmu, T.T., Hockert, K., Holland, E., and Marsella, K., 1999. Petrogenesis of municipal solid waste combustion bottom ash. App. Geochem., 14: 1073-1091.
- Etiegini, L. 1990 .Wood ash as an additive and liming agent. PhD dissertation. Forest products Department. Univ. of Idaho Moscow, Idaho.
- Etiegni, L., Campbell, A., and Mahler, R., 1991. Evaluation of wood ash disposal on agricultural land. I. Potential as a soil additive and liming agent. Commun. In Soil Sci. Plant Analysis 22 (3&4) 243-256).
- Ezeaku, P.I.and Egbemba, B.O. 2014. Yield of maize (*Manoma spp*) affected by automobile waste and compost manure. Afr. J. Biotechnol. 13 (11):1250-1256.
- Ezema, R.A., Ibudialo, A. N., Omeje, T. E., and Chienyinam, G.I., 2013. Evaluation of agronomic performance of Nsukka Yellow pepper (*Capsicum annum L.*) under different rates of boiler ash application in Iwollo, Enugu State ,Nigeria. Proc. 1st Nat. Conf. Crop Sci. Soc. of Nigeria. pp.29-32.
- Faleiros, G.A., Cora, J.E., and Volante, P.R., 2014. Aggregate stability index of Ultisol under sugarcane bagasse ash application. American Soc. Agron. Annual meeting Nov.2-5, 2014 in long Beach, C.A. Papper 139 -143.
- FAO, 1979. World reference base for soil resources. World soil Resources Report 84. Food and Agricultural Organziation of the United Nation, Rome Pp 88.
- FAO, 2000. Fertilizers and their use. A pocket guide for extension officers. Fourth edition. FAO/IFA.70Pp.
- Farhad, W., Sleem, M.F., Chemma, M.A., and Hammad, H.M., 2009. Effect of poultry droppings levels on the productivity of spring maize (Zea mays L.). Jour. Animal and Plant Sci. 19(3): 122-125.
- Fink, D.H., 1970. Water repellency and infiltration resistance of organic-filmcoated soils. Soil Science Society of America Proceedings, 34: 1896194.

- Finkelman, R.B., Belkin, H.E., Zhang, B.C., and Centeno, J. A., 2000. Arsenic poisoning caused by residual coal combustion. In: Proc. 31st Int. Geological Congress ,Guizhou Province, China.
- Foth, H. D. 1990. Fundamentals of Soil Science 8th ed. JOHN WILEY & SONS New York. Pp. 32
- Frech, D., and Smitham, J., 2007. Fly ash characteristics and feed coal properties. Co-operate. Res.centre for coal in sustainable development. Research Report 73:1-55.
- Garampalli, R.H., Deene, S., and Narayana, R. C., 2005. Infectivity and efficacy of Glomus aggregatum and growth response of Cajanus cajan (L.) Millsp. in flyash amended sterile soil. J Environ Biol., 26 (4):70568.
- Garau, M.A., Dalmau, J.L., and Felipo, M.T., 1991. Nitrogen mineralization in soil amended with sewage sludge and flyash. Biol. Fertil. Soils, 12:1996201.
- Gee, G.W., and Bauder, J.W. 1986. Particle size analysis. In: *Methods of Soil Analysis*, Part I. 2nd edition. Klute, A. (ed.). Amer.Soc.Agron., Madison. pp. 383-411.
- GENSTAT, 2009. Discovery Edition. 3 VSN International Ltd.
- Gerlach, R.W., Dobb, D.E., Raab, G.A., and Noccrino, J.M., 2002. Gy sampling theory in environmental studies. Assessing soil splitting protocols. Jour. Chemo. 16:321-328.
- Ghodratic, M., Sims, J.T., and Vasilas, B.S., 1995. Evaluation of fly ash as a soil amendment for the Atlantic coastal plain.1. soil hydraulic properties and elemental leaching.Jour. Water,Soil,AirPollution . 81:349-361.
- Giardini, L., 1991. Aspetti agronomic della gestione dei reflui zootecnici rivista di Ingegnaria Agraria 12:679-689.
- Gibezynska, M., Mellert, E., Stankowski, M., and Woloszyk, S., 2006. Metal content in soil fertilized with brown coal fly ash. Agron. Res. 4(2) 509-516.
- Glardano, P.M., Behel, A.D. Jr., Lawrence, J.E. Jr., Soileau, J.M., and Bradford, B.N., 1983. Mobility in soil and plant availability of metals derived from incinerated municipal refuse. Environ. Sci.Technol.17:193-198.
- Gomez-Barea, A., Vilches, L., Campoy, M., and Fernandez-Pereira, C., 2009. Plant optimization and ash recycling in fluidised waste gasification. *Chem. Eng. J.*, *146*, 2276 236.
- Gorman, J.M., Sencindiver, J.C., Horvath, A., Singh, R.N., and Keefer, R.F., 2000. Erodibility of fly ash used as a top soil substitute in mine land reclamation Jour. Environ. Qual., 29 (3): 805 811.
- Grant, C.A., Buckey, W.T., Bailey, L.D., and Secles, F. 1998. Cadmium accumulation in crops. Cam J. Plant Sci 78:1-17.
- Greenland, D.J., 1977. Soil damage by intensive arable cultivation: temporary or permanent. Phil. Trans. R. Soc. Lond. B, 281:193 208.
- Grewal, K.S., Yadav., P.S., Mehta, S.C., and Oswal, M.C. 2001. Direct and residual effect of fly ash application to soil on crop yields and soil properties. Crop Res.(Hisar). 21: 60-65.
- Gros, R., Poulenard, J., Monrozior, L.J., and Faivre, P., 2006. Soil physico-chemical changes following application of municipal solid water leachates to grasslands. Water, Air and Soil Pollution, 169:81 100.
- Gunse, B., Poschenrieder, C., and Barcelo, J., 2000. The role of ethylene metabolism in the short term responses of aluminium by root of two maize cultivars different in aluminum resistance. Environ., and Expt. Botany 43: 73 81.
- Gupta, A. K, and Sinha, S, 2008. Decontamination and/or re-vegetation of fly ash dykes through naturallygrowing plants. J. Hazard Mater. 153:107861087
- Gupta, D.K., Rai, U.N., Tripathi, R.D., and Inbuhe, M., 2002. Impacts of fly ash on soil and plant responses. Jour. plant Res., 115: 401 409.
- Gupta, A.K., Singh, R.P., Ibrahim, M.H.and Byeong-Kye ,2012. Agricultural utilization of fl y ash and its consequences. In: Eric Lichtfouse (ed) Sustainable agriculture reviews, vol 8. Springer, pp 269. 286
- Gutierrez, B., Pazos, C., and Coca, J., 1993. Characterization and leaching of coal fly ash. Waste Manag. Res. 11 (4), 279 286.
- Haraldsen, T.K., Krogstad, T., 2011. Efficiency of organic NPK fertilizers combining N-rich organic wastes and bottom wood ash. NJF Report 7(8), 50-53.
- Haraldsen, T.K., Brod, E.M., and Krogstad, T., 2012. Quality requirements for wood ash as K
- Hashim, M.A., Mukhopadhyay, S., Sahu, J.N., and Sengupta, B., 2011. Remediation technologies for heavy metal contaminated ground water. Journal of Environ Manage. 92 (10), 2355 2388.
- Haynes, R. (2005).Labile organic matter fractions as central components of the qualityof agricultural soils. An over view. Adv. Agron. 85:221 268.
- Haynes, R.D., and Naidu, R., 1998. Influence of lime, fertilizer and manure applications on soil organic matter content and soil physical conditions: a review. Nutrient cycling in Agro ecosystems, 51: 123 137.
- Haynes, R.J., 2009. Reclamation and re-vegetation of fly ash disposal sites, Challenges and research need. Jour. of Environmental Management, 90:43 53.
- He, P.J. Zhang, H., Zhang, C.G., and Lee, D.J., 2004. Characteristics of air pollution control residues of MSW incineration plant in Shanghai. J. Hazard Mater. 116: 229 237.
- HORIBA, Scientific, 2016. Particle Characterization. 1996.-2016. Horiba, Ltd.
- Huang, H., Campbell, A.G., Folk, R., and Mahler, R.L., 1992. Wood ash as soil additive and liming agent for wheat field studies. Commun. Soil Sci. Plants Anal. 23:25 33.

- Huang, S.J., Chang, C.Y., Mui, D.T., Chang, F.C., Lee, M.Y., and Wang, M.F., 2007 sequential extraction for evaluating the leaching behavior of selected elements in the municipal solid waste incineration fly ash. Hazard mater. 149:180-188.
- Huang, W., 1990. The use of bottom ash in Highway Embankments, sub grades and sub-bases. Publication FHWA/IN/JHRP-90/04. Indian Department of Transportation and Purdue University, West Lafayette, Indiana.
- Hunt, R., 1990. Basic growth analysis. Unwin. Hyman London, Sydney, Boston. pp. 112.
- Igwe, C.A.,2004. Soil properties influencing stability of structure of B- horizons of Ultisols in Semi-arid Nsukka, Eastern Nigeria. Arid Land Research and Maanag.18: 185-195
- Ikpe, F.N., Isimirah, N.O., and Ogbonna, I.J., 1997. Maize growth and nutrient uptake in acid soil of Niger Delta, Nigeria. Niger Delta Biologia, 2:119 124.
- Inam, A., 2007. Use of fly ash in turnip (Brassica rapa L.) cultivation. Pollut. Res. 26 (1): 43 47.
- Jacobson, S.U., Sikstran, M., and Nohrsteu, H.O., 2000. Effects of previous high N addition on nutrient conditions in above ground biomass of Picea abies stand in Sweden, Scand. Jour. For. Res., 15: 30 38.
- Jala, S., 2005. Fly ash as an amendment agent for soil fertility. Ph.D. Thesis, 2005
- Jala, S., and Goyal, D. 2006. Fly ash as a soil ameliorant for improving crop production-a review. Bioresour. Technol., 97: 1136-1147.
- James, K.A., Thring, R.W., Hell, S., and Ghuma, H.S., 2012. Ash management Review: Application of biomass bottom ash. Energies (5): 3856–3873.
- Jamil, M., Qasim, M., and Subhan, A., 2004. Impact of organic waste (Baggasse ash) on the yield of wheat (Triticum aestivum L.) in a calcareous soil. Int. Jour of Agric., and Biology. 6 (3): 468–470.
- Jayalakshmi, M.J., Pushp, K., and Murthy, P., 2007. Fly ash improves soil fertility. The Hindu online edition Indians National Newspaper.
- Jazen, H.H., Larney, F.J., and Olson, B.M., 1992. Soil quality factors of problem soils in Alberta. Proceedings of the Alberta Soil Science Workshop 17 28.
- Jena, P.K., Panigrahi T., Mohanty, B., Das, M., Dash, M.K., and Panda, R.B. 2013. Utilization of paper mill fly ash for sustainable crop production: Effect on the growth of corn (Zea mays L.) and soil properties Discovery Nature 5(13): 15-19.
- Jouyban, Z., 2012. The effects of salt stress on plant growth tech. Jour. of Engineer., and Applied Sci. 2 (1): 7-10.
- Kahl, J., Fernandez, I., Rustad, L., and Peckenham, J.,1996. Threshold application rates of wood ash to an acid forest soil. J.Environ. Qual. 25: 220-227.

- Kalra, N., Jam, M.C, Joshi, H.C, Choudhary, R.C., Harith, J. Vasta, V.K., Sharma, S.K., and Kumar, V., 1998. Fly ash as a soil conditioner and fertilizer. Bioresource Technology, 64:163 167.
- Kalra, N., Harit, R.C., Sharma, S. K.,2000. Soil properties of texturally variant soils. Bioresour. Technol. 75:91-93.
- Kalra, N., Joshi, H.C., Chaudhary, A., Choudhary, R., and Sharma, S.K., 1997. Impact of fly ash incorporation in soil on germination of crops. Bioresource Tech. 61: 39-41. Elsevier science limited.
- Karmakar, S., Mittra, B.N., and Ghosh, B.C., 2009. Influence of industrial solid wastes on soilplant interactions in rice under acid lateritic soil.World of coal ash (WOCA) conference may 4-7 in Lexington.
- Karpate, R.R., and Choudhary, A.D., 1997. Effect of thermal power stations waste on wheat. Jour.Environ.Biol.18 (1):1-10.
- Katiyar, D., Singh, A., Malaviya, P., Pant, D., Singh, P., Abraham, G., and Singh, S.K.,2012.
 Hupact of Fly-Ash-amended soil on growth and yield of crop plantsø, *Int. J.Environment and Waste Management*, Vol. 10, Nos. 2/3, pp.1506162.
- Kayode, G.O and Agboola, A.A., 1993. Investigation on the use of macro and micro nutrients to improve maize yield in southeastern Nigeria. Liming Res., 4:211 221.
- Kemper, A., and Rosenau, K., 1986. Aggregate stability and size distribution. (2nd ed.) In:
 Klute A.(ed) Methods of Soil Analysis. Part 1. Physical and Mineralogical methods.Vol.1.
 Soil Sci. Soc. of America, Madison, Wisconsin, USA pp. 422 425.
- Kene, D.R., Lanjewar, S.A., Ingole, B.M., and Chaphale, S.D., 1999. Effect of application of fly ash on physico chemical properties of soil. Jour. of Soil Sci., and Crops. 1(1):11 18.
- Khan, A., Jong, W., Jansens, P., Spliethof, H., 2009. Biomass combustion in fludized bed boilers: potential problems and remedies. Fuel process. Technol.90:21 50.
- Khan, M.J., and Qasim, M., 2008. Integrated use of boiler ash as organic fertilizer and soil conditioner with NPK in calcareous soil. Songklanakarin Jour. Sci. Tech. 30(3): 281 289.
- Khan, M.R., and Khan, M.,1996. The effect of fly ash on plant growth and yield of tomatoe. Environmental Pollution,92:105-111.
- Khandkar, U.R., Gangwar, P.C., Srivastava, P.C., Singh, M.,1993.õEdaphological characteristics of unweathered and weathered fly ashes from Gondwana and lignite coal. Environmental Pollution. 79: 297-302.
- Kingery, W.I., Wood, C.W., Delaney, D.P., 1993. Impact of long term application of boiler litter on environmentally related soil properties. Journal of Environ. Qual. 8:.211 215.
- Kishor, P., Gosh, A.K., and Kumar, D., 2010. Use of fly ash in Agriculture: A way to improve soil fertility and its productivity. Asian Journal of Agricultural Research 4:1-4.

- Klien, D.H.,andren, A.W., Carter, J.A., Emery, J.F., Fieldman, C., Fulkerson, W., Lyon, W.S., Ogle, J.C., Tahmi, Y., Van Hook, R.I., and Batton, N., 1975. Pathways of thirty seven trace elements through coal-fired power plants. Environ. Sci. Technol. 9:973-979.
- Klutes, A.,1965. Laboratory measurement of hydraulic conductivity of saturated soils. In. Methods of Soil Analysis. Part 2 C.A black et al. (eds) AM. Soc. Agron. 9:210 221.
- Kneeling, A.A., Paton, I.K., and Mullet, J.A.J , 1994. Germination and growth of plants in media containing unstable refuse-derived compost. Soil Biol. Biochem 26: 767-772.
- Korcak , R., 1996. õScrap construction gypsum utilizationö. The Gypsum Association Washington D.C. 31 July, 1996.
- Krakow, E., 2010. Effects of fly ash and stabilized ash on wheat, Daphnia magna, radish and lettuce in laboratory tests. Uppsats för avläggande av naturvetenskaplig magisterexamen Miljövetenskap 30 hp Institutionen för växt- och miljövetenskaper, Göteborgs universitet
- Krejsl, J., A: and Scanlon, T.M., 1996. Evaluation of beneficial use of wood-fired boiler ash on Oat and bean growth. Jour. Environ. Qual. 25:950-954.
- Krishna, R., Punjawane, J., and Kalpana, S. 2013. Effect of sugarcane waste on soil properties of coal fly ash affected land in cultivation of Solanum melongena. Jour. Chem. Bio. Phy. Sci. sect. C. Vol. 3 (2) 1613-1622.
- Kuchanwar, O.D., Matte, D.B, and Kene, D.R., 1997. Evaluation of graded doses of fly ash and fertilizers on nutrient content and uptake of groundnut grown on vertisol. Jour. Soils, Crops 7(1):1-3.
- Kumar, N., 2002. Growth response in crops in fly ash amended soil. Pollution Res., 21:409-416
- Kumar, R., 2004. Genetic monitoring of microbes in soils amended with fly ash M.Sc. Thesis in Department of Biotechnology and Environmental Sciences, Thapar Institute of Engineering and Technology (Deemed University) Patiala.
- Kumar, V., 1998. Fly ash as a soil conditioner and fertilizer. Bio-resource Techno. 64: 163-167.
- Kupper, H, Kupper F., and Spiller M. (1998). In situ substitution of heavy metal substituted chlorophylls in water plants. Photosyth. Res. 58:123-133.
- Lal, R., 1979. Physical properties and moisture retention characteristics of some Nigeria soils. Geoderma 21: 209-223.
- Lam, C. H. K, Alvin, W.M. Ip., Baford, J.P., and McKay, G., 2010. Use of incineration MSW Ash: A Review. Sustainability 2, 1943-1968.
- Larsson, P.E., and Westling, O., 1998. Leaching of wood ash and lime products: Laboratory study. Scand. J. For. Res. Suppl. 2:17622.
- Lau, S.S., and Wong, J.W.C., 2001. Toxicity evaluation of weathered fly-ash amended mature compost.ö Water, Air & soil pollution, 128: 243-254.
- Lee, S.B., Lee, Y.B. and Lee, C.H., 2008. Characteristics of boron accumulation by fly ash application in paddy soil. Bioresource Technol.199: (13): 5928-5932.

Lerner, B.R., and Utzinger, J.B., 1986. Wood ash as soil liming material. Hortscience 21:76-78.

- Levy, G.J. and Torrento, J.R., 1995. Clay dispersion and macroaggregate stability as affected by exchangeable potassium and sodium. Soil Science. 160:3526358.
- Li, H., Peng, X.H., Wu, L.S., Jia, M.Y.and Zhu, H.L.,2009. Surface potential dependence of the Hamaker constant. Journal of Physical Chemstry. C.; 113: 441964425.
- Li, S., Li, H., Xu, C.Y., Huang ,X.R., Xie, D,T.and Ni. J.P., 2013 Particle interaction forces induce soil particle transport during rainfall. Soil Science Society of America Journal.; 77: 156361571.
- Amézketa E., 1999. Soil Aggregate Stability: A Review. Journal of Sustainable Agriculture. ;14:263, 836151.
- Lima, A.T., Ottosen, L.M., Perdersen, A.J., and Rebeiro, A.B., 2008. Characterization of fly ash from bio and municipal waste. Biomass and bioenergy, 32 (3), 277-282.
- Lindasy, W.L., and Norvell, W.A., 1978. Development of DPTA soil tests for Zn,Cu, Fe, and Mn. Soil Sci. Amer.Jour.42:421-428.
- Liu, E., Yan, C., Mei, X., Zhang, Y., and Fan, T., 2013. Long term effect of manure and fertilizer on soil organic carbon pools in dry land farming in Northwest China. PLOS one 2013.8(2):e56536.Published on line2013 Febuary, 20. doi:10-1371
- Liu, X.B., Han, X.Z., Herbert, S.J., Xing B. 2003. Dynamics of soil organic carbon under different agricultural management systems in the black soil of China. Commun. Soil Sci. Plant Anal., 34: 9736984.
- Logan, T. J., and Chaney, R. L., 1983. Utilization of municipal wastewater and sludge on landó metals. *In* Proceedings of the Workshop on Utilization of Municipal Wastewater and Sludge on Land. pp. 2356326.
- Lopez, R., Padilla, E., Bachmann, S., and Eichler Locbermann, B., 2009. Effect of biomass ashes on plant nutrition in tropical and temperate regions. Jour. of Agric., and Rural Devt. in the tropics and sub-tropics. 110 (1): 51-60.
- Lopez, R., Padilla, E., Bachmann, S., and Eichler Locbermann, B., 2009. Effect of biomass ashes on plant nutrition in tropical and temperate regions. Jour. of Agric., and Rural Devt. in the tropics and sub-tropics. 110 (1): 51-60.
- Lucas, E.O., 1984. Effect of population density on yield and dry matter partition of maize varities in Nigeria. Indian. Jour. Agric. Sci., 54: 284-290.
- Magdoff, R., Bartett, R., and Ross, D., 1984. Wood ash research project (Burlington Electric Dept.). Final Report, Dept. Plant and Soil Sci. Uni. of Vermont, Burlington.
- Mahmood, S., Finlay, R. D., Fransson, A.M., Wallander, H., 2003. Effects of hardened woodash on microbial activity, plant growth and nutrient uptake by ectomycorrhizal spruceseedlings. FEMS, Microbiology Ecology. 43, 121-131.

- Mahmood, S., Finlay, R.D., Fransson ,A.M., and Wallander, H., 2003. Effect of hardened wood ash on microbial activity, plant growth and nutrient uptake by ectomycorrhizal spruce seedlings FEMS Microbial. Ecol.43:121-131.
- Maiti, S.K., Singh, G., and Srivastava, S.B., 2005. Study of The Possibility of Utilizing Fly Ash for Back Filling and Reclamation of Opencast Mines: Plot and Field Scale Study With Chandrapura Fly Ash, Fly Ash India, New Delhi
- Majldzadeh, K., EL-Mitiny, R.N., and Bokowaska. A.,1977. Power plant bottom ash in black base and bituminous surfacing. Vol.2. Userøs manual, Federal Highway Administration Report No. FHWA-RD-78-148, Washington D.C.
- Mallik, A.U.,Gimingham, C.H., and Rahman,A.A.,1984. Ecological effects of leather burning.1.water infiltration, moisture retention porosity of surface soil. Jour.of Ecology. 72:767-776
- Manitoba, 2013. Effects of manure and fertilizer on soil fertility and soil quality. Pp 39.
- Marschner, H., 1996. Mineral nutrition of higher plants. Ann. Bot. 78 (4): 527 -528.
- Martens, D.C., 1971. Availability of plant nutrient in fly ash. Compos. Sci. 12:15-19.
- Mass, E. V., 1990. Crop salt tolerance. in: K. K. Tanji, ed., Agricultural Salinity Assessment and Management, Manual on Engineering Practice No. 71, American Society of ChemicalEngineering, New York, pp. 2626304. material. TAPPIJ. October 1986. 114-119.
- Matte, D.B., and Kene, D.R. 1995. Effect of fly ash application on yield performance of kharf and rabi crops. Journal of Soils and Crops, 5: 133-136.
- Mattigod, S.V., Dhanpat, R., Eary, L.E., and Ainsworth, C.C., 1990. Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residues. i. review of major elements. J. Environ. Qual.19: 188-201.Maximizing Soil Productivity. Food Products Press, Binghamton, NY.
- Mbagwu, J.S.C., Bazzoffi, P., and Unamba-Oparah, I., 1994. Physico-chemical and mineralogical properties influencing water-stability of aggregates of some Italian surface soils. Paper presented at College on Soil Physics held at Trieste Italy in June, 1994. IC /94 /105.
- Mbagwu, J.S.C., 1985. Subsoil productivity of an Ultisol in Nigeria as affected by waste and inorganic fertilizer in a severely degraded sandy soil in Southern Nigeria, Bio resource Technology 51: 117-123.
- Mbagwu, J.S.C., 1989. The agricultural soils of Nigeria: properties and agronomic significance for increased productivity. Beitr. Trop. Landwirtsch Veterinarmed 27:395-409.
- Mbagwu, J.S.C., 1995. Saturated hydraulic conductivity in relation to physical properties of soils in the Nsukka plains, Southeastern Nigeria. Geoderma 68:51 66.

- Mbah, C. N., Nwite, J.N., Njoku, C., and Nweke, I. A., 2010. õResponse of maize (*Zea mays* L.) to different rates of wood-ash application in acid ultisol in Southeast Nigeria,ö African Journal of Agricultural Research, vol. 5, no. 7, pp. 5806583, 2010.
- Mbah, C. N., Oguejiofor, C. U., Idike, F. I., Nwovu, I.G., and Attoe, E.E., 2013. Changes in Rheological Properties and Heavy Metal Content of an Ultisol amended with ash and its effect on maize yield. Nig. J. Biotech. Vol.25: 53 -59.
- Mbah, C.N., and Nkpaji, D., 2010. Response of Maize (Zea mays L.) to different rates of wood ash in acid Ultisol in Abakaliki Southeastern Nigeria. Jour. of American Soil Sci. 6 (1):53-57.
- Mbah, C.N., Mbagwu, J.S.C., Onyia, V.N., and Anikwe, M.A.N., 2004. Effect of application of biofertilizers on soil densification, total porosity, aggregate stability and maize grain yield in a dystric leptosol at Abakaliki. Nigerian Journal of Soil Science, 16: 145 150.
- Mc- Bride, M.B., 2002. Toxic metals in sewage sludge-amended soils: has promotion of beneficial use discounted the risk? Advances in Environmental Research xx (2002) xxxxxx.
- Mc- carthy, G.J., Johansen, S.,and Steinwand, S.J., 1987. öCorrelations of chemistry and mineralogy of western US fly ashö. Material Research Society proceedings Vol.86, Puttsburgh, Pa. PP 109-112.
- Mckeague, J.A., Wang C., and Topp, G.C., 1982. Estimation of saturated hydraulic conductivity from soil morphology. Soil Sci. Soc. Am J. 49: 1239 1244.
- McLean, E. O., 1982. Soil pH and lime requirement. In: Methods of Soil Analysis, Part 2, 2nd ed. (Agronomy Monograph 9), ed. A. L. Page et al., 1996224. Madison, Wisc. ASA and SSSA.
- Meller, E., 1999. Changes in the properties of sandy soil fertilized with different doses of ashes from -*A*Dolna Odra*ø* power station Florida University of Agriculture Research Station, 78:189–202.
- Metson, A.J., 1961. Methods of Chemical Analysis of Soil Survey Samples. Govt. Printers, Wellington, NewZealand, Pp.207.
- Miller,S., and Rahe,T.M.,1988.Utilization of boiler ash as a by product of agricultural lime substitute. Tappi Proceedings.1990 Environmental Conf.
- Mira, M., Raglund, R., and Baker, A., 1993. Wood ash composition as a function of furnace temperature. Biomass and Bioenergy 4 (2): 103-116.
- Mittra, B.N., Karmakar, S., Swain, D.K., and Ghosh, B.C., 2003. Fly ash- a potential soil amendment and a component of integrated plant Nutrient supply system. FUEL 84:1447-1451.

- Mladenov, M., Serafimova, E. K., and Pelovski, Y., 2011. Examinations on granulation of soilimprovers on the basis of biomass ashes. J. of Environmental Protection and Ecology, 12 (4A): 2198 - 2204.
- Mohammadi, K., and Rokhzadi, A., 2012. An integrated fertilization system of canola (Brassica napus L.) production under different crop rotations. Industrial Crops and Products, 37 (1): 264-269.
- Molliner, A.M., Street, J.J., 1982. Effect of flyash and lime on growth and composition of corn (Zea Mays L.) on acid sandy soils. Proc. Soil crop Sci. FL 41:217-20.
- Montes-Hernandez, G., Perez-Lopez, R., and Renard, F., 2008. Mineral sequestration of CO₂ by aqueous carbonization of coal combustion fly-ash. Jour. Harzard Mater.18 (2-3): 347-54).
- Moore, P.A., Jr., and Miller, D.M., 1994. Decreasing phosphorus solubility in poultry litter with aluminum, calcium, and iron amendments. Journal of Environmental Quality 23:3256330.
- Mueller Warrant, G.W., Mellbye, M.E., and Aldrich Markham, S.,1991. Pronamid improves weed control in new grass plantings protected by activated charcoal.Jour. Applied Seed Prod., 9: 16 26.
- Muse, J.K., and Mitchell, C.C., 1995. Paper mill boiler ash and lime byproducts as soil liming materials. Agron. J. 87:432-438.
- Nair, V.D.; Graetz, D.A.and Dooley, D.O., 2003. Phosphorus release characteristics of manure and manure-impacted soils. Food Agric. Environ., 1:217-223.
- Nasir, M.N.and Qureshi and M.A. 1999. Response of sugarcane to bio-compost prepared from filter cake and stillage.Pak. J. Soil Sci. 16 : 75-80.
- Natusch, D.F.S., and Wallace, J.R., 1974. Urban aerosol toxicity: the influence of particle size. Science 186:695.
- Nelson, D.W.and Sommers, L. E.,1982. Total organic carbon, organic matter. In: Page et al.. (eds.).Methods of Soil Analysis. Part 2.Agron.9 ASA, SSSA Madison W.I. pp. 539 579.
- Niemeyer, T., Niemeyer, M., Mohammed, A., Fottner, S., and Haøardtle, W., 2005. Impact of prescribed burning on nutrient balance of Health lands with particular reference to nitrogen and phosphorus. Appl. Veg. Sci. 8: 183–192.
- Nigussie, A., Kissi, E., Misganaw, M., and Ambaw, G., 2012. Effect of biochar application on soil properties and nutrient uptake of lettuce (Lactuca sativa) grown in chromium polluted soils. Am. Euro. Jour. Agric. & Environ. 12 (3) 369 376.

- Nottidge, D.O., Ojeniyi ,S.O., Asawalam, D.O., 2007. Effect of different levels of wood ash on nutrient contents of maize (*Zea mays* L.) and grain yield in an acid Ultisol of Southeast Nigeria. Nig. Jour. Soil Sci. 17:98-103.
- Novoa, R., and Loomis, R.S., 1981. Nitrogen and plant nutrition. Plant Soil 58: 177-204
- Nurmesniemi, H., Makela, M., Poykio, R., and Dahl, O., 2011. Comparison of fertilizer properties of ash fractions from medium-sized (32 MW) and small ósized (6MW) municipal district heating plants. World Acad. Sci., Engineer., and Tech. 51:1143-1147.
- Nwachukwu, O.I., Nyong, A.E., and Opara, U.D. 2012. Effect of manures and ash on soil properties, yield and nutrient uptake of Amaranthus in an Ultisol of South east Nigeria. Nigeria J. of Soil Sc. 22 (2): 70-78.
- Nwite, J.C., Igwe, C.A., and Obalum S.E., 2011. The contribution of different ash sources to the improvement in properties of a degraded Ultisol of southeastern Nigeria. American-Eurasian Jour. of Sustainable Agric.5 (1):34-41
- NSWEPA, 1997. Environmental guidelines: use and disposal of biosolids products. (EPA, Sydney.)
- Obalum, S.E., Oppong, J., Igwe, C.A., Watanabe, Y., and Obi, M.E., 2013. Spatial variability of uncultivated soils in derived savanna.Int.Agrophys.27:57-67.
- Obernberger, I.,1997. Aschen aus biomassfeuerunaen. Zusammensetzung und verwertung VDI-Berichte Dusseldorf, 1319:199-222.
- Obi, M.E., and Ebo, P.O., 1995. The effect of organic and inorganic amendments on soil physical properties and maize production in a severely degraded sandy soil in southern Nigeria. Bioresource Technology, 51: 117-123.
- Ojeniyi ,S.O., Awanlemhen, B.C., and Adejoro ,S.A. 2010. õSoil plant nutrients and maize performance as influenced by oil palm bunch ash plus NPK fertilizerö Jour. of American science. 6 (12): 456-460.
- Ojeniyi, S.O., Ezekiel, P.O., Asawalam, D.O., Awo, A.O., Odedina, S.A., and Odedina J.N., 2009. Root growth and NPK status of cassava as influenced by oil palm bunch ash. African Jour. Biotech. 8 (18): 4407-4412.
- Oku, E., Essoka, A., and Thomas, E., 2010. Variability in soil properties along an Udalf toposequence in the humid forest zone of Nigeria. Kasetsart. J. (Nat.Sci), 44.564-573.
- Okunade, E.A., 2010. Geotechnical properties of some coal fly ash stablished southwestern Nigeria lateritic soils.Morden Applied Jour. 11(12):66-73.
- Ologunde, O.O., 1974. Effect of nitrogen and population on yield and yield components of maize (Zea mays). M.sc. Thesis. Graduate School, University of Missouri ó Columbia, Missouri. Pp. 164.

- Oluwatosin, G.A., and Ogunkunle, A.O., 1991. Suitability rating of some soils of the savanna zone of southwestern Nigeria for maize production. Nigerian Journal of Soil Science., 10: 1-24.
- Ombo, F. I.,1995. Self-sufficiency in local fertilizer production for Nigeria. In: Proceeding of 3rd African Soil Science Society Conference (August 20 23,1994) at University of Ibadan, Nigeria.
- Onweremadu, E.U., Ibeawuchi, I.I., and Duruigbo, C.I., 2008. Land evaluation and productivity of organically fertilized crop mixtures in degraded tropical soil. Nature and Science 6 (1): 34-41.
- Onwuka, M.I., Osodeke, V.E., and Ano, A.O.,2009. Use of liming materials to reduce soil acidity and affect maize growth parameters in Umudike, South East Nigeria. Production Agriculture and Technology 5 (2): 386-396.
- Orajiaka, S. O.,1975. õGeologyö, Nigeria in maps. Eastern states.(ed) G.E.K. Ofomata. Ethiope Publ. House, Benin city Nigeria.
- Orhue, E.R., and Izunwanne, C.L., 2013. Heavy metals status of soil and their uptake by fluted pumpkin (Telferia occidentals Hook F) cultivated along Ikpoba river bank. Benin City. Nigeria Jour. of Soil Sci. 23(1): 102-109.
- Orhue, E.R., Erhayimwen, M., and Ekhom, A.M., 2011. Heavy metal concentrations in soils and some crops grown on waste dump sites in Benin City, Nigeria. The Nigerian Journal of Agriculture and Forestry, 2(2): 167-178.
- Osodeke, V.E., and Ano, A.O., 2009. Use of liming materials to reduce soil acidity and affect maize growth parameters in Umudike, South East Nigeria. Production Agriculture and Technology, 5 (2): 386-396.
- Page, A.I., R.H. Miller and D.R. Keeney, 1982. *Methods of Soil Analysis*. Partó2. 2nd Ed. Agron. 9, Madison, Wisconsin, USA
- Page, A.L., Elseewi, A.A., and Straughan, I.R., 1979. Physical and chemical properties of fly ash from coal-fired power plants with special reference to environmental impacts. Residue Rev. 71:83-120.
- Pandey, V.C., and Singh, N., 2010. õReview: Impact of fly ash incorporation in soil systems, Agriculture,ö Ecosystems & Environment, vol. 136 no. 1-2, pp.16-27.
- Pankaj, K. J., Panigrahi, T., Mohanty, B., Das, Dash, M. K., and Panda, R.B., 2013. Utilization of Paper Mill Fly Ash for Sustainable Crop Production: Effect on the growth of Corn (*Zea mays* L.) and Soil Properties. *Discovery Nature*, 5(13), 15-19.
- Papadimitriou, C. A., Haritou, I., Samaras, P., and Zouboulis, A. I., 2008. Evaluation of leaching and ecotoxicological properties of sewage sludge-fly ash mixtures. Environ Res. 106 (3) 340-8.

- Parbhu, M., Veeraraghavthatham, D., and Srinwasan, K., 2003. Effect of nitrogen and phosphorus on growth and yield of eggplant hybrid COBH-1. South Indian Horticulture, 51(1-6): 152-156.
- Pathak, H., Kalra, N., Sharma, S., and Joshi, H. C., 1996. Use of fly ash in agriculture: Potentialities and constraints. Yojana, 40, 6 24-25.
- Pathan, S. M., Almore, L. A. G., and Colmer, T. D., 2003.õProperties of Several Fly Ash Materials in Relation to Use as Soil Amendmentsö, Journal of Environmental Quality, Vol. 32, 2003, pp. 687-693.
- Pathan, S. M., Almore, L. A. G., and Colmer, T. D., 2003.õProperties of Several Fly Ash Materials in Relation to Use as Soil Amendmentsö, Journal of Environmental Quality, Vol. 32, 2003, pp. 687-693.
- Pati, S. S., and Sahu, S.K., 2004. CO₂ evolution and enzyme activities (dehydrogenase, protease and amylase) of fly ash amended soil in the presence and absence of earthworms (Drawida willsi, Michaelsen) under laboratory conditions. Geoderma, 118: 289-301.
- Patterson ,S. 2001. The agronomic benefitof pulp mill boiler wood ash. An M. SC. Thesis submitted to the School of Graduate Studies Council of the University of Lethbridge, Lethbridge, Alberta, Canada.
- Pattnaik, G., 1992. Monitoring control and disposal management of fly ash vis-a -vis pollution abatement in NTPCøs stations. ENCONEN 47-54.
- Peech, M. 1965. Hydrogen-ion activity, in C.A. Black, Ed., *Methods of Soil Analysis*, Part 2. Agronomy Number 9, American Society of Agronomy, Madison, WI, 9146926.
- Petruzzelli, G., 1989. Recycling wastes in agriculture: Heavy metals bioavailability. Agric. Ecosyst. Environ. 27:493-503.
- Petruzzelli,G., Lubrano, L., and Cervelli,S.,1986. Heavy metal uptake by wheat seedling grown on fly ash amended soils. J. Environ. Qual .8: 171-175.
- Phil-Eze, P.O., 2010. Variability of soil properties related to vegetation cover in a tropical rainforest landscape. Jour. Geogr. Reg. Plan. 3: 177-184.
- Phung H.T., Lund, L.J., and Page, A.L., 1978. Potential use of fly ash as a liming material. In: Adriano D.C., and I.L. Brisbin (eds). Environmental Chemistry and Cycling Processes. Conf. 760429. Department of commerce,. Springfield, V.A: US Pp. 504-515.
- Prabakar, J., N. Dendorkar and R.K. Morchhale, 2004. Influence of fly ash on strength behavior of typical soils. Constr. Build. Mater, 18: 263-267
- Prabhu, M., Veeraraghavathatham, D., and Srinivasan ,K., 2003. Effect of nitrogen and phosphorus on growth and yield of eggplant hybrid COBH-1. South Indian Horticulture 51(1-6):152-156.
- Praharaj, C.S., Bandyopadhyay, S., and Sankaranarayanan, K., 2007. Integrated nutrient management strategies for increasing cotton productivity. Model training course on ocultivation of long staple cotton (ELS)ö December 15-22, 2007. Central inst. For cotton Res. Reg. Stat. Coimbaton.

- Pujari, G.K., and Dash, P.M., 2006. Problem and management aspects. Environ. Newsletter Environ. Centre Environ. Stud. 3(1):1-8.
- Quaak, P., Knof, H., and Stassen, H., 1999. Energy from biomass, A Review of combustion and Gasification Technologies. World Bank Washington DC, USA.
- Raison, R. J., 1979. Modification of the soil environment by vegetation fires, with particular reference to nitrogen transformation. A Review. Plant Soil, 51: 73-108.
- Ram, L.C., Mastro, R.E., Singh, S., Tripathi, R.C., Jha, S.K., Srivastava ,N.K., Sinha, A.K.,Selv, V.A., and Sinha, A., 2011. An appraisal of coal fly ash soil amendment technology (FASAT) of central institution of mining and fuel research (CIMFR) world Academy of Sci, Engineer., and Tech. ,52:703-714.
- Ram, L.C., Srivastava, N.K., Jha, S.K, Sinha, A.K., Masto, R.E., and Selvi, V.A.,2007. õManagement of lignite fly ash through its bulk use via biological amendments for improving the fertility and crop productivity of soil.ö Environmental Management, Vol. 40:4386452.
- Ram, L.C., Srivastava, N.K., Tripathi, R.C., Jha S.K, Sinha, A.K, Singh, G., and Manoharan, V., 2006. Management of mine spoils for crop productivity with lignite fly ash and biological amendment. Jour. Environ. Manag.79:173-187.
- Ram, L.C, Tripathi, P.S.M., and Mishra, S.P., 1995. Iron-bearing minerals in bituminous and semi anthracitic Indian coals: Moessbauer spectroscopic characterization and studies on their transformations during ashing and carbonization/ devolatilisation. In: Narsimhan, K.S., Sen, S. (Eds.), Proc. Golden Jubilee Int. Symposium -Coal Science Technology Industry Business and Environment Coal, 96:38-57.
- Rani, K., andKalpana, S., 2010. Utilization in agricultural and related field, a better alternative for ecofriendly maintenance of coal fly ash. Journal of Chemical and Pharmaceutical Research, 2(5): 365-372.
- Rasken, I., Smith, R.D., and Salt, D.E., 1997. Phytoremediation of metals: Using plants to remove pollutants from the environment. Current opinion in Biotechnology, 8: 221-226.
- Rautaray, S.K., Gosh, B.C., Mittra, B.N., 2003. Effect of fly ash organic waste and chemical fertilizer on yield, nutrient uptake, heavy metal content and residual fertility in a ricemustard cropping sequence under lateritic soils. Bioresour. Technol. 90:275-83.
- Reynolds, W.D., 1993. Saturated h ydraulic conductivity. Field measurement. In: Soil sampling and Methods of Analysis, ed. M.R. Carter, 599 613. Canadian Soil Sci.Ann. Arbor, Mich., Lewis.
- Rhoades, J.D. 1996. Salinity: electrical conductivity and total dissolved solids, in R.L. Sparks, Ed. *Methods for Soil Analysis*, Part 3, *Chemical Methods*, SSSA Book Series Number 5, Soil Science Society of America, Madison, WI, 4176435.
- Richards, L.A., 1954. Diagnosis and improvement of saline and alkali soils. Washington: US Department of Agriculture. USDA Agricultural Handbook, 60

- Rifa, L A., Yasufuku, N., and Tsuji, K., 2009. Characterization and effective utilization of coal ash as soil stabilization on road application. Ground improvement Technologies and Case Histories Edited by C.F Leung et al., pp 469-474.
- Rohriman, F.A., 1971. Analyzing the effect of fly ash on water pollution. Power, 115,76.
- Roy, R.N., Finck, A., Blair, G.J., Tandon, H.I.S., 2006. Plant nutrition for food security. A guide for integrated nutrient management. FAO Fertilizer and Plant Nutrition. Bulletin 16:pp.164.
- Roy, W.R., Thiery, R.G., and Schuller, R.M. ,1981. Coal fly ash: a review of the literature and proposed classification systems with emphasis on environmental impacts. Environmental Geology Notes 96. Champaign, IL: Ilinois State Geological Survey.
- Saarsalim, A., Malkonen, E., and Pirainen, S., 2001. Effects of wood ash fertilization on forest soil chemical properties.ö Silva Fennica 35 (3): 355-368.
- Saarsalimi, S., Hedley, M.J., and White, K.O., 2001. A simplified resin membrane technique for extracting phosphorus from soil. Fertilizer Res. 24: 173-180.
- Sadasivan, S., Meenakshy, V., Negi, B.S., and Nambi, K.S.V.,1993. Chemical characterization and leaching tests on fly ash from a coal fired thermal power plant. Nat Seminar on Environmental Aspects of Thermal Power Plants, NTPC, Noida, UP, December 1993.
- Saidur, A., Abdelaziz, E., Demirbas, A., Hossain, M., Mekhilef, S., 2010. A review on biomass as a fuel for boilers. *Renew. Sustain. Energy Rev.*, 15, 226262289.
- Sajwan, K. S., Ornes, W.H., and Youngblood, T.V., 1996. Growth and elemental composition of sorghum Sudan grass grown in fly ash: organic waste amended soils. J. Environ Sci. Health. Part A.31: 1729-1739.
- Sambo, A. S., 2009. Prospects of Coal for Power Generation in Nigeria. A Paper Presented at the International Workshop on Promotion of Coal for Power Generation, Held at the Nike Lake Resort Hotel, Enugu on 27th-28th April 2009.
- Sandberg, J., Karlsson, C.,and Fdhila, R., 2011. A 7 year long measurement period investigating the correlation of corrosion, deposit and fuel in a biomass fired circulated fluidized bed boiler. Appl. Energy, 88, 996110.
- Sanwal, S.K., Lakminarayana, K., Yadav, R.K., Rav, N., Yadav, D.S., and Mousumi, B.,2007. Effect of organic manures on soil fertility, growth, physiology, yield and quality of turmeric. Indian Jour. of Hort. 64(4): 444-449.
- Sarangi, P.K., Mishra, T.K., Mishra, P.C., 1997. Soil metabolism, growth and yield of Oryza sativa L. in fly ash amended soil. Indian J. Environ. Sci. 1 (1), 17624.
- Sarkar, A., and Rano, R. 2007. õWater holding capacities of fly ashes: effect of size fractionation,ö Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 29: 4716482.

- Sarkar, A., Rano, R., Mishra, K.K., and Sinha, I.N. ,2005. õParticle size distribution profile of some Indian fly ash: a comparative study to assess their possible usesö Fuel processing Technology, 86: 1221-1238.
- Savage, S.M., Martin, J.P., and Letey, J., 1969. Contribution of humic acid and a polysaccharide to water repellency in sandand soil. Soil Sci. Soc. Am. Proc. 33:149-151.
- Savant, M.K., De Datta, S.K., 1982. Nitrogen transformation in wetland rice soils. Adv. Agron. 35, 241-302.
- Saywan, K.S., Paramasivam, S., Alva, A.K., and Sahi, S.V., 2006. Fly ash organic product mixture as soil amendment. Inj-Twardowska et al.. (eds. Soil and water Pollution Monitoring, Protection and Remediation 3-23.
- Schiemenz, K., and Eichler-lobermann, B., 2010. Biomass ashes and their phosphorous fertilizing effects on different crops. In. Nutri. Cycle Agroecos.87:471-482.
- Schiemenz, K., Kern, J., Paulsen, H., 2011. Phosphorous fertilizing effects of biomass Ashes. Recycling of Biomass Ashes (Eds) H. Insam, B.A. Knapp 17-31.
- Schutter, M.E., and J.J. Fuhrmann, 2001. Soil microbial community responses to fly ash amendment as revealed by analyses of whole soils and bacterial isolates. Soil Biol. Biochem., 33: 1947-1958.
- Selvakumari, G., Baskar, M., Jayanthi, D., and Mattan, K.K., 1999. Fly ash in integrated plant nutrient system and its impact on soil properties, yield and nutrient uptake of groundnut. Madras Agric. Jour. 36:556-561.
- Selvakumari, G., Bhaskar, M., Jayanthi, D., and Mathan, K.K., 2000. Effect of integration of fly ash and fertilizers and organic manure on nutrient availability, yield and nutrient uptake of rice on Alfisols Jour of the Indian Soc. of Soil Sci. 48: 268-278.
- Serafimova, E.K., Mladenov, M., Mihailova, I. Pelovski Y., 2011.Study on the characteristics of waste wood ash.Journal of the University of Chemical Technology and Metallurgy, 46, 1, 2011, 31-34
- Shaheen, S. M., Hooda, P.S., and Tsadilas, C.D., 2014. Opportunities and challenges in the use of coal fly ash for soil improvements A review. Jour. Environ. Manag. 145:249-267.
- Shahi, U.P., Singh, S., Srivastava, B.K., and Singh, M.P., 2002. Effect of nitrogen and phosphorus application on residual soil fertility and yield of hybrid briinjal in mollisol. Vegetable science 29(2): 195-196.
- Sharma, M.P., Tanu, U., Reddy, G., 2001. Herbage yield of Mentha arvensis DC. Holms as influenced by AM fungi inoculation and farm yard manure application grown in fly ash over burdens amended with organic matter. International ash utilization symposium, KY, USA.
- Sharma, S., Sharma, P., and Mehrota , P., 2011. Bioaccumulation of heavy metals in Pisum sativum L. growing in fly ash amended soil. Int. Jour. Agric. & Environ. (2): 1-8.

- Sharma, S.K., and Kalra, N., 2006. Effect of fly ash incorporation on soil properties and productivity of crops: a review J. sci. Ind. Res. 65 (5): 383-390.
- Sharma, S.K., Kalra, N., and Singh, G.R., 2001. Fly ash characteristics and its incorporation effects on germination on maize rice. Jour. Sci. Ind. Res.Vol.60:957-952
- Shaver, E.M., Hansen, C.L., and White, R.K. (1985). The patho-biology of heavy metals to livestock. In:"Agricultural Waste Utilisation and Management". pp.719-728. (American Soc. Agric. Engineers, Michigan, USA.)
- Shortall, J. G., and Liebhardt W. C., 1975. Yield and growth of corn as affected by poultry droppings. J. Environ. Qual. 4 (2): 186-191.
- Shukla, M.K., Tripathi, R.D., Rai, U.N., Dwivedi, S., Chandra, S., Mishra, S., Rai, P., and Dwivedi, S., 2003. Studies on bioutilization of fly ash using leguminous cropsø Abstract: National Symposium on Cyanobacteria and Plants under Environmental Stress: Responses, Defence Strategies and Biotechnological Prospects, B.H.U., Varanasi, p.49.
- Sims, J.T., Vasilas, B.L., Ghodrati, M., 1995. Development and evaluation of management strategies for the use of coal fly ash as a soil amendments. In: Proceedings of the 11th international symposium of the Am Coal Ash Assoc., Orlando, Florida, p. 8.1618.
- Singh, C.B., M.C. Oswal and K.S. Grewal, 2002. Impact of fly ash application on consumptive and water use efficiency in wheat (*Triticum aestivum*) under different soils *Indian J. Agric. Sci.*, 72:39669
- Singh, G., and Kumar, S., 1997. Environmental evaluation on leaching of trace elements from coal ashes: a case study of Chandrapur thermal power station. Jour. of Environ.Stud. & policy, 2 (2), 135-142.
- Singh, L.P., and Siddiqui, Z.A., 2003. Effects of fly ash and Helminthosporium oryzae on growth and yield of three cultivars of rice. Bioresource. Technol. 86: 73-78.
- Singh, N., Yunus, M.,2000. Environmental impacts of fl y-ash. In: Iqbal M, Srivastava PS, SiddiqTO (eds) Environmental hazards: plant and people. CBS, New Delhi, pp 60. 79
- Singh, R.K., and Gupta, N.C., 2014. Value added utilization of fly ash 6 prospective and sustainable solutions. Int. J. of Appl. Sci and Engineer. Res. 3 (1): 1-16.
- Singh, R.P., Das, S.K., Rao, B.U.M.and Reddy, N.M., 1990. Towards sustainable dry land agricultural practices. Central Research Institute Dry land Agriculture, Hyderabad, India.106.
- Singh, S.N., Kulshreshtha , K., and Ahmad, K.J., 1997. Impact of fly ash soil amendment on seed germination, seedling growth and metal composition of vicia faba L. ecological Eng.9:203-208.

- Six, J., Elliott, E.T., and Paustian, K., 2000. Soil structure soil organic matter. 1. A normalized stability index and the effect on mineralogy. Soil Sci. Soc. America. Journal 64:1042 1049.
- Sohi, S.P., Lopez-Capel, E., Krull, E., Bol, R., 2009. Biochar, climate change and soil: A review to guide future research. CSIRO Landand Water Science Report 05/09, 64 pp.
- Sparks, D.L. 1995. Environmental chemistry of soils. Academic Press. New York.
- Steenari, B.M., Marsic, N., Kartsson, L.G., Tomsic, A., and Lindqvist, O., 1998. Long term leaching of stabilized wood ash. Second.J. For. Res. Suppl. :3-1.
- Steponkus, P., 1992. Proceedings, TAPPI Environmental Conference Press Altanta Vol.1 p.33.
- Stevenson, F.J., and Cole, M.A. (1999). Cycles of soils-second Edition. John Wiley and Sons Inc. Pp 427.
- Sushil, S., and Batra, V.S., 2006. Analysis of coal ash heavy metals contents and disposal in three thermal power plants in India. Fuel 85: 2676-2679.
- Suthar, M.R., Singh, G.P., Raria, M.K., and Lal, M., 2005. Growth and fruit yield of brinjal (Solanium melongena L.).as influenced by planting dates and fertility levels. Crop research Hisar. 30 (1): 77-79.
- Taylor, E.M., and Schumann, G.E., 1988. Fly ash and lime amendment of acidic coal soil to aid vegetation. Jour. Environ . Qual. 17:120-124.
- Teaca, C.A., and Bodirlau. R., 2008. Assessment of toxicity of industrial wastes using crop plant assays. BioResources 3(4): 1130-1145.
- Tester, M., Davenport, R. 2003. Na+ tolerant and Na+ transport in higher plants. Annals of Botany, 91: 503-527.
- Thetwar, L.K., Sahu, D.P., Valshnawa, M.M.,2006. Analysis of *Sesamuim indicum* seed oil from plants grown in fly ash amended acidic soil. Asian J. chem. 18 (1): 481-484.
- Thomas, G.W., 1982. Exchangeable cations. In: Methods of Soil Analysis (ed.I.L. Page) ASA Press Madison, WI, USA.
- Thompson, L.M., and Troeh, F.R., 1978. Soils and soils fertility. Mcgran-Hill, New York,516pp.
- Tiecher, T., Zafar, M., Fábio Joel Kochem Mallmann, F.J.K., Bortoluzzi, E.C. Bender, M.A. Ciotti, L.H. and dos Santos, D.R., 2014. Animal manure phosphorus characterization by sequential chemical fractionation, release kinetics and 31p-nmr analysis. R. Bras. Ci. Solo, 38:1506-1514
- Tiwari .A, Dwivedi, A.K., and Dikshit, P.R., 2002. Long term influence of organic and inorganic fertilization on soil fertility and productivity of soybean-wheat system in a Vertisol. Jour. Indian Soc. Soil Sci. 50: 472-475.
- Toor, G.S.; Peak, J.D. and Sims, J.T., 2005. Phosphorus speciation in broiler litter and turkey manure produced from modified diets. J. Environ. Qual., 34:687-697.

- Tripathi, R.D., Vaipayee, p., Singh, N., Rai, U.N., Kumar, A., Ali, M.B., and Yunus, M. 2004. Efficacy of various amendments for amelioration of fly-ash toxicity: Growth performance and metal composition of Cassia Siamea Lamk. Chemosphere. 54 (11), 1581-1588.
- Tripathy, A., and Sahu, R.K., 1997. Effect of coal fly ash on growth and yield of wheat. J. Environ Biol. 18 (2): 131-135.
- Tsadilas ,C.D. 2014. Agricultural use of fly ash: Expected benefits and consequencesWACAU-2014, Israel International Workshop on Agricultural Coal Ash Uses.27 ó 29 May 2014
- Tsadilas, C.D., Samaras, V., Kazai, P., Sgouras, J., 2002. Fly ash and sewage sludge application on an acid soil and their influence on some soil properties and wheat biomass production. In: Proceedings of the 2002, vol. III. International Soil Conservation Organization, Beijing, China, pp. 118e123. May 26e31, 2002.
- Ugwu, D.S., 2006. Crop production in the compound farming system of southeastern Nigeria. Jour. of Agric., and Soc. Res.(JASR) 6 (1):1-10.
- Unamba-Oparah, I., 1985. The potassium status of the study soils northern Imo State of Nigeria. Soil Sci., 139:437 445.
- USPA .,2007. The use of soil amendment for remediation, revitalization and reuse. Super fund Remediation and Emergency Response. EPA 542-R-07-013.
- USDA SCS 1974. Soil Classification System. Definition and Abbreviations for Soil Description. West Technical Service Center, Portland, Oregon, USA.
- Van Herck, P.V., and Vandecasteele, C., 2001. õEvaluation of the use of a sequential extraction procedure for the characterization and treatment of metal containing solid wasteö. Waste Manage. 21: 685-694
- Vance, E.D., 1996. Land application of wood fired and combination ashes. An overview .J. Environ. Qual. 25:937-944.
- Vershinin, P.V., 1939. Metody Operedeleniya razmyvaemosti pochi pri pomoschi ob øektwongo nefelomiton (Determination of water erodibility of soils by means of objective nepheometer). Doklady Vaskhnil No. 8: 1939.
- Vest, M.M., Chirenje, P.E., and Ma, L.Q., 1999. Study of slash pine response to wood fired boiler ash and fertilizer in a woodfired boiler ash amended soil. PhD Thesis, Department of Soil and Water Science University of Florida Gainesville, FL 32611-0290.
- Vincini, M., Carini, F., Silva, S., 1997. Use of alkaline fly ash as amendment for swine manure. Bioresour. Technol. 49: 213-222.
- Wange, S.S., and Kale, R.H., 2004. Effect of biofertilizer under graded nitrogen levels on brinjal crop. Journal of Soils and Crops, 14(1): 9-11.
- Wolf, B. 1990. The Fertility Triangle: The Interrelationship of Air, Water, and Nutrients inWong, J. C., Yiang ,R.F., and Sil, D.C, 1996. Boron Availability in ash-Sludge Mixture and its Uptake by Corn Seedling Soil Science 161: 182-187.
- Wong, M.H., and Wong, J.W.C., 1989. Germination and seedling growth of vegetable crops in fly ash amendment soils. Agric. Ecosyst. Environ. 26.23-25

- Wong, W., Gorsuch, J. W., and Lower, W.R., 1991. Plants for toxicity assessment. ASTM STP 1091,ASTM Philedelphia.
- Yeledhelli, S., Prakash, S.S., Gurumurthy, S.B., and Ravi, M.V. 2007. Coal fly ash as modifier of physico-chemical and biological properties of soil. Karnataka J. Agric. Sci. 20(3): 531-534.
- Yolou, I., Tovihoudji, G.P., Batamoussi, H.M., Yabi, I., Paraiso, A.A., Akiyo, R., and Afouda, F., 2015. Short- term effects of conjuctive use of municipal solid waste compost and inorganic fertilizer on soil properties and maize productivity in Northern Benin. Int. Res. Jour. Agric. Sci and Soil Sci., 5 (6): 137-149.
- Yoshida, I., and Padre Jr., B.C., 1975. Effect of organic matter application and water regimes on the transformation of fertilizer N in Phillipine soil. Soil Sci., Plant Nutri. 21: 281 292.
- Yoshida,H., Shimamura, K., and Alzawa, H., 2007. õ3R strategies for the establishment of an international sound material-cycles society.ö Jour. Mater. Cycles. Waste Manage.9, 10111.
- Yunusa, I.S.M, Burchett M.D, Manpharan V., Lionel De silva, D., Eamus, D., and Greg, S. C., 2009. Photosynthetic pigment concentration, Gas exchange and vegetative growth for selected monocots and dicots treated with two contrasting coal fly ashes. J. Environ. Qual. 38: 466-1472.
- Yunusa, I.A.M., and Gworgwor. N.A., 1991. Growth and yield analysis of maize genotypes during dry seasons in northern Nigeria. Exp. Agric. 27:3976405.
- Yunusa, I.A.M., Manoharan, V., DeSilva, D.L., Eamus, D., Murray, B.R. and Nissanka N.P. 2008. Growth and elemental accumulation by canola on soil amended with coal fl y-ash. J. Environ. Qual. 37:126361270.
- Zimmermann, S. and Frey, B., 2002. Soil respiration and microbial properties in an acid forest soil: Effect of wood ash. Soil Biol. Biochem.34:1727-1737.
- Zucconi, F., Pera, A., Forte, M., and Bertoldi, M., 1981. Evaluating toxicity of immature compost. Biocycle , 22: 54-57.

APPENDICES

APPENDIX I: TERMINOLOGY OF ASHES AND COMBUSTION METHODS

Boiler ash is a generic term applied to many types of ash produced by the burning of various materials. There are 4 general types of boiler ash commonly available, each with its own chemical and environmental characteristics.

Wood Ash ó from boilers where wood (or bark) is used as a heating source. Coal Ash ó from coal powered electrical generating power plants, actually of two forms, bottom ash and fly ash.

Tire Ash ó produced from burning shredded tires for fuel in generating plants.

Incinerator Ash ó produced from burning MSW (Municipal Solid Waste, i.e. Garbage) as a waste disposal method.

According to Swedish Thermal Engineering Research Institute (Varmeforsk), bottom ash; fly ash and APC residue (air pollution control residue) are the only three categories used today to describe an ash. Bottom ash is the ash extracted from the lowest part of the furnace while fly ash consist of the particles that because of their small size or their low density, have been carried over by the combustion gases and fall out in various parts of the boiler and the flue gas cleaning system.

Ash is the mineral non-combustible part of a fuel, including impurities such as sand or gravel. In the flue gas cleaning system reagents are injected to remove pollutants. These reagents are e.g lime for desulphurization of the flue gases or active carbon to bind dioxins or mercury. The mixture of fly ash and residues from these reagents is called APC residue.

GRATE COMBUSTION OF FLUDIZED BED COMBUSTION

The woods boiler and furnace are often used interchangeably, but this is not the same piece of equipment.

FURNANCE: is the part of a õboilerö where the fuel is burned.

BOILER: is the part where the heat of combustion is delivered to a water/steam circuit. The word boiler is often used for the combustion of both units.

GRATE FURNANCE: here the solid fuel is pushed onto a grate and combustion air is provided from below and through the grate. The fuel is dried, it is carbonized and then burns out

on the grate. What is left of the fuel, ash, falls over the edge of the grate and is carried away as bottom ash. The gases produced during carbonization are burned above the grate.

FLUDISED BED BOILER: In FBB, the velocity of the air flow through the bed is high and the fuel hovers in the gas flow. All three purchases (drying, carbonizing and burning-out) go on in the same volume. Additional materials like sand are used to make the bed hovering at all stages of combustion.

BUBBLING FLUDISED BED (BFB): In BFB, the gas velocity is moderate and the bed stays in place in the furnace.

CIRCULATING FLUDISED BED (CFB)

In a CFB, the gas velocity is high enough to carry fuel and bed materials out of the furnace. The bed materials is separated from the combustion gases in a cyclone downstream and returned to the furnace.

An oversized material which cannot be suspended in the gas flow is extracted from the bottom of the BFB or CFB as bottom ash or bed ash.

PULVERISED FUEL BOILER/FURNANCE (PFB)

Here the fuel is ground to a powder, per-mixed with air and injected into the furnace. It is common for coal fuels but not common for solid biofuels.

Ash from a grate furnace or PF furnace consists only of ash from the fuel and whatever impurities came with it. Ash from a fluidized bed furnace consists of both fuel ash and spent bed material.

BOILER ASH: Ash that is carried over by the combustion or flue gases will fall out on low points in the ducts or when there are obstacles. The ash that fall out as the flue gases pass through the boiler is known as boiler ash. Occasionally, it is regarded as fly ash.

CYCLONE ASH/FILTER ASH/ESP ASH: After the boiler the flue gases are led to the flue gas leaning system before leaving through the Chimney stack. DE dusting will take place in one of several types of equipment.

-cyclones removing particles above 1000m

-ESP or electrostatic precipitation where particles are charged in an electric field and captured by the electrodes, removing particles down 0.1mm and reduces dust content $10-50 \text{mg}/4\text{m}^3$.

-**Bag house filters**, where dust is captured in textile filters or ceramic inserts, removing the fine particles and reducing the dust content to -35mg/Nm³.

A material called fly ash may be called cyclone ash, ESP ash or filter ash if one wishes to keep apart the different types of equipment. All three types are seldom used together in one system. However, one type or two types in combination may be used: e.g. ESP only or cyclone and baghouse filter in succession. Occasionally, boiler ash is regarded as part of the fly ash.

DESULPHURIZATION ASH: In order to reduce the sulphur concentration, one may inject an absorbent in the flue gases. This may be lime or sodium hydrogen carbonate. The spent absorbent and fly ash known as (APC residue) is collected in a bag house filter.

: In practice, several flows of ash are collected together. The bottom ash will then be a mixture of three types of ash. It may be difficult to describe the ash more precisely than bottom ash, fly ash or APC residue if the exact arrangement of the ash extraction is not known.



APPENDIX: III: Solive Vegetable Oil Mills Limited Boiler Ash Landfill Disposal sites at Oduru Nsukka, Enugu State, Nigeria.



Plate 1



Plate 2: Solive Vegetable Oil Mills Limited Boiler Ash Landfill Disposal sites at Oduru Nsukka, Enugu State, Nigeria.

Ca^{2+} Mg^{2+} K^+	Na (cmol/kg)	Class
<2 <0.3 <0.2	<0.1	very low
2 5 0.3 1 0.2 0.3	1 0,3	low
5 10 1 3 0.3 0.6	0.3 0.7	moderate
10 20 3 8 0.6 1	0.7 2	high
>20 >8 1.2 2	>2	Very high

APPENDIX IV: Interpretation Guide for Evaluating Analytical Data.

(a) Exchangeable cations

(b) Cation exchange capacity (CEC)(Cmo1/kg)

Range	Class
<6	Very low
6 12	low
12 25	moderate
25 40	high
>40	Very high

(c) Percentage Base Saturation (%)

Range	Class
0 20	Very low
20 40	low
40 60	moderate
60 80	high
>80	Very high

(d) Hydraulic conductivity (USDA SCS 1974)

Range (cm/hr)	Class
<0.13	Very slow
0.13 0.51	Slow
0.51 2.0	Moderate slow
2.0 6.3	moderate
6.3 12.7	Moderate rapid
12.7 25.4	Rapid
>25.4	Very rapid

(e) Organic matter rating and interpretation by Metson (1961)

Range (%)	Class
<2	Very low
2 4	Low
4 10	Medium
10 20	High
>20	Very high

(f) Soil pH rating by Metson (1961)

Range	Rating
<4.5	Extremely acidic
4.5 5.0	Very strongly acidic
5.1 5.5	Strongly acidic
5.6 6.0	Moderately acidic
6.1 6.5	Slightly acidic
6.6 7.5	Neutral
7.4 7.5	Slightly alkaline
7.9 8.4	Moderately alkaline
8.5 9.0	Strongly alkaline
>9.0	Very strongly alkaline

(g) Total Nitrogen rating by Metson (1961)

Range (%)	Class
<0.1	Very low
0.1 0.2	Low
0.2 0.5	Medium
0.5 1.0	High
>2.0	Very high

(h) Organic Carbon

Range (%)	Class
<0.4	Very low
0.4 1.0	Low
1.0 1.5	Moderate
1.5 2.0	High
>2.0	Very high

(i) Available Phosphorous

Rating by Enwezor *et al.* (1989)

Bray	1	Bray 2	
Range (ppm)	Class	Range (ppm)	Class
<8	Low	<15	Low
8 20	Medium	15	Medium
>20	High	25	High
>25	Very high	>25	Very high

Metal (mgkg ⁻¹)	WHO (Hungarian) ^a	FEPA
Cd	1	NA
Со	30	NA
Cr	75	NA
Zn	200	NA
Cu	30	NA
Pb	100	NA
Ni	40	NA
V	NA	NA
Mn	NA	NA
Fe	NA	NA

(j) Standards (permissible limits) of heavy metals as prescribed by WHO (Hungarian baseline value (threshold limit) and Nigerian soil (FEPA threshold limit value).

a:Hungarian Government Regulation Number 10/2000,NA= not available.

APPENDIX V: Danish Legislation relating to Wood ash Application (2001)

1. No recycling of wood ash with Cd content over 15 ppm. Specifically, no fly ash. Three classes of content are designated of which content of 0.5-8.0 is the mid point.

2. Other heavy metal contents are restricted to Pb: 120 ppm, Hg: 0.8 ppm, Ni:30-60 ppm,Cr:100 ppm

3. P content shall be limited to a maximum of 30 kg/ha or total of 90 kg/ha over three years.

4. No more than 7.5 Mg of wood ash may be applied to a stand over a single rotation, with a lower limit if the Cd content is relatively high (upper band).

5. Analysis for polyaromatic hydrocarbons (PAH) must be made where residual carbon content is over 5%.

PAH content must not exceed 3mg/kg (From SkogForsk Report No.2, 2001