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Agronomic potentials of boiler ash derived from oil palm wastes as fertilizer, soil amendment, and liming materials.

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ABSTRACT

One potential problem with recycling power plant ashes is its variability both from fuel to fuel and within a certain fuel-type. This study obtained information on the main components of ashes derived from burning oil palm mill wastes in boilers for energy generation to obtain reference data for the development of its utility possibilities with particular emphasis on use as fertilizer, soil amendment, and liming materials. The physical and chemical properties of the boiler ash (BA) were analyzed and their test values and properties were compared with those of poultry droppings. This comparison provides information necessary for judging their suitability in comparison with widely used poultry droppings. The results show that BA has predominately sand-sized particles, with small bulk density (0.32 Mg cm^{-3}); high electrical conductivity (433.8 d/s/cm), and pH (9.2). The chemical composition of the ash was dominated by macro-elements Ca, K, Mg, P, but are also enriched with micro-elements such as Fe, B, Zn, and Mn, The BA compared favorably with poultry droppings except in nitrogen content but has higher substantial value as an agricultural lime substitute. The results suggest that the BA may be useful for fertilizing and liming, given their phytonutrient concentrations and neutralization potentials. However, its low nitrogen content and high electrical conductivity are a concern in situations of high application rate.

1.0 Introduction

Waste utilization as secondary raw materials resources has been considered as the best option of pollution prevention and disaster risk management strategy. Biomass wastes are currently burnt in boilers for producing steam and generating electricity. Such practice produces a residue in form of boiler ash (BA) which contains the bulk of the mineral fraction of the original biomass (Khan *et al*, 2009). Given the global focus on waste recycling and bio-energy development, the use of biomass in energy generation has been on the increase and as a result, the production of boiler ash has continued to increase (James, 2012). The management of boiler ash as derived from burning oil palm mill wastes in boilers has attained an apparent scenario for scientific and strategic concern in Nigeria due largely to the country's prominence in oil palm production.

.Generally, boiler ash consists of salt, oxides, and hydroxides of Ca, Mg, and K and traces quantities of micronutrients and trace metals extracted from the soil during plant growth (Campbell, 1990). According to Catricalla *et al,* (1996), Khan and Qasim, (2008); and Ezema *et al.,* (2013); agriculture provides a feasible alternative for safe disposal of BA to improve the soil environment and enhance crop productivity. In this way, a significant part of the macro- and micronutrients taken by the plants returns to the soil, closing the circulation of minerals. However, they can contain harmful substances, such as heavy metals (Catricalla *et al.,* 1996).

Inferences drawn from previous studies indicate that ash characteristics are variable and depend to a large extent on the type and origin of plant species from which the ash is generated (Demirbas, 2005, Vassilev *et al*. (2015). These factors can enrich or reduce the content of elements in biomass ash. Therefore, to develop an operational plan for

its use, the ash characteristics must be assessed.
Kalembkiewicz, *et al.* (2019) researched industrial wood ash to assess its posed threats and possible applications. Also, Zajac *et al*. (2018) researched to obtain information on the main components of ashes from 35 biomass species used in combustion processes to obtain reference data for the development of utility possibilities for these ashes, with particular emphasis on agricultural use. They concluded that the potential use of ash from each type of biomass in the aspect of its chemical composition should be considered individually, regardless of the division into groups depending on the origin of biomass.
The characteristics of ash produced from burning oil palm mill wastes in boilers have not been assessed. Because of the above, the assessment of the characteristics of ashes generated from the combustion of oil palm wastes in boilers becomes a very important problem.
Based on laboratory investigation, this study assessed the properties of boiler ash derived from burning oil palm mill wastes that are likely to affect its use as fertilizer, soil amendment, and liming materials. Specifically, this involved determination of its physical properties, nutrient and salt contents, and liming value and comparing them with some characteristics of commonly used poultry droppings.
The results obtained from this study will provide valuable information that will improve our capacity to recommend and implement protective management practices concerning land application of BA generated from burning oil palm mill wastes (OPBA).

2.0 Materials and methods

2.1 Sample Collection and Preparation
The boiler ash used in this study was a composite sample of fly and bottom ash produced from the biomass-fired heat combustion system in Solive Vegetable Oil Mill Ltd Nsukka, Enugu State, Nigeria, being the product of combustion of palm kernel shells, cake, sludge, and empty fruit bunches on an inclined sliding grate.
A sampling of the ashes was carried out over a period of three days and the individual samples (1kg per sampling day) were combined into one composite sample with a weight of 3kg. The sampling period represented normal process operating conditions for the combustion plant e.g. in terms of oxygen content and temperature. The ash was transported to a laboratory and dried at room temperature for 14 days until getting to an air-dried state. A coning and quartering method (Gerlach *et al.,* 2002) was repeatedly applied to reduce the ash samples to a size suitable for conducting laboratory analysis.
2.2 Physicochemical Characterization of Biomass Ash Samples
The physicochemical properties of the ash were determined according to standard procedures used for characterizing combustion by-products.
2.3 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 into 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.

2.4 Bulk density of boiler ash and poultry droppings
The method of self-compacting (Brazil, 2007) was used to determine the bulk density of BA and PM. A 500 ml plastic beaker was filled to the 300 ml mark with the substrate. Then, this cylinder was lifted and dropped 10 times, falling under the action of its weight from a height of 10 cm.

$$= (\text{mass at saturation} - \text{oven dry mass}) / \text{mass of boiler ash or poultry droppings only} \times 100.$$

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 the dry weight. The procedure was repeated three times using different subsamples.
2.5 Saturation moisture percentage of boiler ash and poultry droppings

This was calculated using the formula,
Saturation moisture percentage
2.6 Electrical conductivity (EC)
Electrical conductivity (EC) was determined by the method described by Rhoades (1996). 10g each of the samples was weighed for analysis. 25ml of deionized water was added to the weighed soil sample and stirred. The EC values were obtained using an electrical conductivity meter.
2.7 Chemical Composition of Boiler Ash and Poultry droppings
pH and Phosphorous
Marking the pH of ash and PM was carried out in distilled water (pH = 7). Measuring pH was performed using a properly calibrated Beckman Zeromatic pH meter. Available phosphorus was determined by the Bray II method as described by Bray and Kurtz (1945).
The Boiler ash and poultry droppings samples (10 g) were mineralized with HNO3 (conc.) and HClO4 (conc.) mixtures in a volumetric ratio of 2:1 (33 mL:16.5 mL). The process was carried out in a Teflon crucible on a hot plate (HP 88720-26 Barnstead/Thermolyne, USA) until full evaporation of acid mixtures was achieved. Each sample was filled with distilled water after cooling down, filtering through a quantitative filter, being acidified with 2 M HNO3, and made up to the mark with water. Mineralization was carried out in triplicate. Content of metals (Ca, Cd, B, Fe, K, Mg, Mn, Pb, Zn) in received effluents was determined with the use of flame atomic absorption spectrometry (FAAS). Contents of carbon and nitrogen were determined with the direct elemental analysis and the use of an elemental analyzer (Vario EL III Elementary, Germany).
Liming value ($CaCO_3$ equivalent) was measured by neutralization. 0.5g of boiler ash sample was gently boiled with 50ml of 0.5ml HCl in 300ml conical flask for 5mins. The mixture was allowed to cool and 3 drops of phenolphthalein indicator were added and titrated against 0.5ml NaOH to the endpoint (pH8.0). a similarly boiled control containing only 0.5ml HCl was prepared as a blank.
2.8 Statistical Analysis
All laboratory analyses were performed in triplicate and their results were subjected to descriptive statistical analysis.

3.0 Results and Discussion

3.1 Physical properties of oil palm 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 1.

The sieve analysis of the boiler ash showed that it 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}. 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 a density value of 0.49 Mgm^{-3}.

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 may change soil 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 the surface texture of ashes significantly affects their 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 ashcan 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 a nutrient release.

The density of BA (0.374 Mgm^{-3}) obtained from burning oil palm wastes was very low compared to that of bituminous coal (0.93 Mgm^{-3}), paper mill ash (1.01 Mgm^{-3}), or bagasse ash (1.95 Mgm^{-3}) (Aigbodion et al. 2010; Mladenov et al, 2011). It is about 6% lighter than the poultry droppings. In comparison to the poultry droppings, its lower bulk density is likely to increase the potential for dust formation, which may create problems in its transportation and storage in dry conditions. A study by Grau *et al.* (2015) indicated that the bulk density of biomass ash in an uncompressed state decreases along with decreasing waste grain diameter which in addition to the absence of cohesiveness explains the reason for their high susceptibility to dusting.

Table 1: Particle size, Bulk density, and Saturation moisture content (S.M.C) of the boiler ash and poultry droppings (Number of samples = 3)

		Boiler ash		Poultry droppings	
Particle size	Unit	Mean Value	Standard Deviation	Mean Value	Standard 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
Electrical conductivity	d/s/cm	433.8	18.26		

The saturation moisture content of the OPBA (77 % on a weight basis) was very high compared to that of the 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 probably due to its high electrical conductivity. It should, however, be noted that the analyzed material has hygroscopic properties that cause the grains to stick together, forming aggregates that tend to reduce in size either by vibration or other processes. These properties may influence the uniformity of application in the field.

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 2. 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%. The analyzed boiler ash contains 12.5 % of unburnt carbon, which indicates a high content of biomass char. The result was in line with that of Huang *et al.* (2014) which observed lower values of unburnt carbon in ash from the combustion of deciduous wood chips than from coniferous trees. It was lower than that of the poultry manure (43.5%), indicating that the associated undesirable organic compounds (e.g. polycyclic aromatic hydrocarbons) in the ash may below. Therefore, the prescribed reduction of carbon before field application which may be cost and resource prohibitive may not be necessary (Gomez-Bare et al., 2009). 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 a decrease in mineral nitrogen level.

The total nitrogen (0.20 mg kg^{-1}} contents of the ash were lower than that of the poultry droppings ((4.15 mg kg^{-1}). 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 and PM were 1-147-5 and 25-5-1 respectively. The calcium concentration of the boiler ash and poultry droppings was 1.5 and 4.77 $Cmolkg^{-1}$ respectively. The concentration of Mg^{2+} (7.2 $Cmolkg^{-1}$) and K^+ (10.56 $Cmolkg^{-1}$) were higher in the ash than in the poultry dropping which was - Mg^{2+} (4.77 $Cmolkg^{-1}$) and K^+ (6.7 $Cmolkg^{-1}$). C: N ratio of the BA and PM was 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 pH of oil palm boiler ash (OPBA) was below the reported range (from 9 to 13.5) combustion by-products from woody biomass reported in the literature (Etiegni, 1991; Serafimova *et al.*, 2011; Schiemenz *et al*., 2011, Kalembkiewicz *et al.* 2018) except that obtained from coal (Katiyar *et al*. 2012). This implies that it has lower liming potentials than most of the ashes and 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 soils (Van herck and Vandacastleele, 2001). Therefore, the application of the BA to soil may enable farmers to grow a much wider range of crops more cost-efficiently.

Table 2: Chemical properties of boiler ash and poultry droppings (3 Samples)

Properties	Units	Boiler ash	Standard Deviation	Poultry droppings	Standard Deviation
pH (H_20)		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
$CaCO_3$ equivalence	%	35.7		21.3	

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

The acid-neutralizing value (NV) measured, as calcium carbonate equivalence is one of the important indices in evaluating the liming effect value of ash about its use in agriculture. According to Saarsalami (2001), the capacity of a liming agent to neutralize soil acidity depends on the levels of soluble and hydrolyzable 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 the loss of carbon during the combustion of the biomass in the boilers. Therefore, the addition of the ash in the 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 a 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). On contrary, Obernberger (1997) noted that higher P availability could be expected from agricultural biomass ashes such as bagasse ash than from wood 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 is 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.

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.

3.3 Micronutrient 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 a soil amendment. Table 3 shows the content of Mn, Zn, Fe, Bo, Pd, and Cd in the BA and PM. Manganese content of the BA (17.5 mg kg^{-1}) was 22 times higher than that of the PM (0.92 mg kg^{-1}) and 4 times higher in Zn. However, the Fe content of the PM (167 mg kg^{-1}) was 31 times higher than that of the BA (16.09 mg kg^{-1}). The cadmium content of the BA and PM were 16.71 and 29.27 mg kg^{-1} respectively, while, their lead content was below detection.

Table 3: Micronutrient and heavy metal content of the boiler ash and poultry droppings

Element	Unit	Boiler ash	Standard deviation	Poultry droppings	Standard 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
B	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

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

High Cd content in soils may pose many environmental and health concerns due to its ability to bio-accumulate within the 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

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 phytotoxicity 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 the 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 a need to assess their impact on soil and crop productivity

4.0 Conclusion

The key characteristics of boiler ash generated from oil palm mill wastes on their use in agriculture as fertilizer, soil amendments, and liming materials were assessed. It has low bulk density, high water holding capacity and porosity, rich sand-sized particles, alkaline nature, and reasonable plant nutrients. It also compared favorably with poultry droppings except in nitrogen content. Its high electrical conductivity is a concern in situations of high application rate but has a substantial value as agricultural lime. Therefore, its use as fertilizer requires further and detailed research with long-term monitoring of its impact on soils.

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