Original Research Article

Comparative Study of Selected Macro and Micronutrients in Bio slurry Samples from different Feed stocks and Inorganic Fertilizers

Abstract

In Kenya overuse of inorganic fertilizers have rendered soils in arable areas acidic leading to poor crop production and hence great risk of food insecurity. An alternative source of plant nutrients that can also address soil acidity is needed if the country is to be food secure. Bio slurry, a by-product from the biogas plant, can successfully be used to improve crop productivity and soil health. This study was conducted to determine the levels of macro and micro nutrients in bio-slurry from different feed stocks and compare with nutrients from conventional chemical fertilizers. Physical parameters were determined on site. The samples were digested using protein digestion method for nitrogen and acid digestion method for phosphorus, potassium, sodium and magnesium. Phosphorus was then determined using UV-Vis while metals a flame emission spectrophotometer was used. The levels of macro and micronutrients were found to be significantly high in bio slurry samples than in select inorganic fertilizers. This study indicates that bio slurry has basic pH and can be used to raise the pH of acidic soil upon prolonged application. In addition, pig waste slurry can serve better as a planting fertilizer due to its high P content while Cow dung slurry would best serve as a top dresser due to the high nitrogen content.

Keywords: Bio slurry; Fertilizer; Micronutrients; Macronutrients; Food security

Background

Poor soil fertility and nutrient depletion are huge obstacles facing farmers in Africa and ending of poverty in most citizens who depend on agriculture as a source of income. In Kenya, decline in soil fertility is a primary constraint to agricultural production. There are poor agricultural practices that have led to soil nutrient depletion, such as farmers applying incorrect and insufficient soil inputs. Farmyard manure is still the main way for managing soil fertility in Kenya but it is usually insufficient in quantity and poor in quality (Mugwe *et al*., 2009).

Inorganic fertilizers are supplementary to the nutrient cycle. Production of inorganic fertilizers require significant energy input and results in generation of large amount of residual waste treatment products whose nutrient-rich nature is not exploited. Anaerobic digestion of organic waste promotes enhanced cycling of nutrient resources through nutrient rich end products and presents an alternative to the energy demanding generation of mineral fertilizers (Arthurson, 2009).

Bio-slurry fertilizer is increasingly becoming a valuable product of anaerobic digestion. As a fertilization agent, digested organic waste is recycled back to arable land, which ensures that crops receive the majority of the essential nutrients for growth. The use of bio-fertilizer has also been linked in conservation of soil fertility and improvement of soil structure and humus balance. This promotes the closure of natural nutrient and energy cycles (Arthurson, 2009).

Anaerobic digestion produces two main outputs: biogas and bio slurry (the digestate or digester effluent). While biogas is used to produce energy, the large potential of bio slurry has often been overlooked (Groot and Bogdansk, 2013). A particularly nutrient-rich fertilizer is obtained if dung and urine is digested. Compared with solid sludge from fermented straw and grass, the liquid slurry is rich in nitrogen and potassium. The solid fermentation sludge, on the other hand, is relatively richer in phosphorus. A mixture of solid and liquid fermented material gives the best yields (Njogu *et al.,* 2015).

Bio-fertilizers offer a new technology to agriculture holding a promise to balance many of the shortcomings of the conventional chemical based technology. Bio-fertilizer is generally incorporated into the soil before planting or, after dilution with water, sprayed directly onto vegetables and fruit crops during the growth period (Groot and Bogdansk, 2013).

Inorganic fertilizers supply essential plant nutrients, mainly nitrogen (N), potassium (K) and phosphorous (P). These fertilizers increase the yield of the crop but they cause several health hazards, hence consumer preferences have shifted towards the use of the organic food grown without use of any chemical. Bio-fertilizers are low-cost renewable source of nutrient that supplements the chemical fertilizer. Plants need different nutrients for growth and enzymatic processes (Warnars and Oppenoorth, 2014). They also need a certain climate and soil composition. The soil consists of physical, biological and chemical aspects. The last of these can be divided into nutrient availability, pH value, cation exchange capacity (measuring fertility), oxidation reduction and salinity. Mineral nutrition includes the supply, absorption and utilization of essential nutrients for growth and yield of crop plants. Macro (e.g. carbon, nitrogen, oxygen, calcium) and micro (iron, manganese, chlorine) nutrients are equally important for a plant and its growth rate. A plant consists of 42% carbon, 44% oxygen, 7% hydrogen and 7% nutrients (of which nitrogen and potassium account for the largest part). The higher the yield of a plant, the higher the uptake of nutrients. A plant can experience deficiency as well as nutrient absorption and assimilation problems.

There are 14 essential plant nutrients. Carbon and oxygen are absorbed from the air while other nutrients including water are typically obtained from the soil (exceptions include some parasitic or carnivorous plants). Plants must obtain mineral nutrients from the growing media. The primary macronutrients are nitrogen (N), phosphorus (P), potassium (K). The three secondary macronutrients are calcium (Ca), sulfur (S), magnesium (Mg). The micronutrients/trace minerals are boron (B), chlorine (Cl), manganese (Mn), iron (Fe), zinc (Zn), copper (Cu), molybdenum (Mo), nickel (Ni). The macronutrients are consumed in larger quantities and are present in plant tissue in quantities from 0.2% to 4.0% (on a dry matter weight basis). Micro nutrients are present in plant tissue in quantities measured in parts per million, ranging from 5 to 200 ppm, or less than 0.02% dry weight (USEPA, 2010).

Materials and methods

Sample collection and pre-treatment

Samples for this study were collected from Githunguri sub-county, Kiambu County in Kenya. The site was chosen due to intensity of biogas technology adoption by dairy farmers in the sub-county. Miniature biogas digesters were set up at Jomo Kenyatta University of Agriculture and Technology and the digesters were fed with cow dung, chicken litter and swine waste and allowed to undergo anaerobic digestion. Bio slurry samples were collected from the digesters and stored in clean plastic bottles. The undigested manure samples were also collected and stored in clean, sealable and airtight bags. Inorganic fertilizers; DAP ETG ®, CAN from Yara ®, Urea-Mea ® and NPK –Falcon, were procured from an agrochemical shop in Juja town. The slurry was sieved and the liquid content analysed for the dissolved nutrients. Physical parameters of the samples (pH, EC and TDS) were determined on site.

Fig 1: Miniature Biogas digesters set up at JKUAT

The undigested manure samples were allowed to dry in the air at 35 °C and relative humidity of 30 – 60 percent for 24 hours and ground using a mortar and pestle to increase the surface area.

The following codes were used for the selected samples:

GR- raw cow dung from Githunguri (Slurry before feeding digester)

GD- digested cow dung slurry from Githunguri

CD – cow dung slurry sample Jkuat mini digester

CH- Chicken litter slurry Jkuat mini digester

PG – Pig waste slurry Jkuat mini digester

UREA, NPK, CAN and DAP – inorganic fertilisers

Determination of total phosphorous

1ml of concentrated sulphuric acid and 5ml concentrated nitric acid were added to 50ml of the sample. The mixture was heated on a hot plate and reduced to a volume of 1ml (where the solution became colourless) to remove nitric acid. The digestate was cooled and 20ml distilled water, 0.5 ml phenolphthalein indicator solution were added. To this solution, 1N sodium hydroxide solution was added until a faint tinge colour was produced. The solution was then transferred to 100ml volumetric flask and distilled water added to the mark. Standard solutions were prepared using the same procedure as the sample.

10ml of the digested samples, blank and standard solutions were pipetted into 100ml beakers and 10ml of molybdivanadate solution added. To the resulting solution 25ml of distilled water was added into each beaker, mixed and allowed to stand for at least 5min. The percentage transmittance for each solution were measured at 430nm using a Shimadzu UV-Vis 1800.

Determination of total nitrogen

To 1.5g of the sample, 0.5g copper sulphate, 5.0g potassium sulphate and 15ml concentrated sulphuric acid were added and digested for 90min using protein digester. The digestate was topped up 100ml volumetric flask mark with distilled water.

Then 10ml of the diluted digestate was measured and 15ml of 40% sodium hydroxide was added. The mixture was distilled in 25ml 4% boric acid and 1ml mixed reagent indicator and topped to 60ml using distilled water. The distillate was then titrated with 0.02N HCl.

The background of this method is that nitrogen content is estimated by titration of the ammonium borate (formed after sample reaction with boric acid) with standard sulphuric or hydrochloric acid, using a suitable indicator to determine the end-point of the reaction.

$$H_2BO_3^- + H^+ \rightarrow H_3BO_3$$

The concentration of hydrogen ions (in moles) required to reach the end-point is equivalent to the concentration of nitrogen that was in the original food. The following equation was used to determine the nitrogen concentration of a sample that weighs *m* grams using a *x*M HCl acid solution for the titration:

$$\% N = \frac{x \text{ moles}}{1000 \text{ cm}^3} \times \frac{(v_s - v_b) \text{ cm}^3}{m \text{ g}} \times \frac{14 \text{ g}}{\text{moles}} \times 100$$

Where *v*s and *v*b are the titration volumes of the sample and blank, and 14g is the molecular weight of nitrogen N. A blank sample is usually analysed at the same time as the material being analysed to take into account any residual nitrogen which may be in the reagents used to carry out the analysis. Once the nitrogen content has been determined it is converted to a protein content using the appropriate conversion factor:

% Protein = F %N.

Determination of Sodium, Magnesium and Potassium

1 gram was weighed and mixed with 12 ml of aqua regia and 3 ml of hydrogen peroxide. The contents were heated on a hot plate at 85 °C until the volume reduced to 5 ml. Upon cooling the

contents were topped up to 50 ml using deionized and analysed using a flame atomic emission spectrophotometer (Borges *et al*., 2003).

Exchangeable potassium was extracted using 1N neutral ammonium acetate at pH 7 (Pratt, 1965) before analysis.

RESULTS

Physical parameters of Bio slurry

Table 1: Physical parameters of Bio slurry

Physical parameters of Bio slurry			
SMP	pH	Conductivity (mS/m)	TDS (ppm)
CDS1	7.5	13.42	7625
CDS2	7.6	13.50	8550
CDS3	7.9	14.22	9088
PGS1	7.5	21.10	16242
PGS2	7.8	21.60	13824
PGS3	8.4	22.40	14336
CHS1	7.7	15.10	10112
CHS2	7.8	14.80	9472
CHS3	8.1	15.80	9856
G1D	7.5	15.63	8350
G1R	7.4	18.00	9690
G2D	7.7	15.93	8650
G2R	8.0	15.25	8350
G3D	7.4	13.03	7110
G3R	7.6	17.67	9570

Cow dung slurry from JKUAT digesters had a mean pH of 7.67, pig waste slurry had a mean pH of 7.9, chicken litter slurry a mean pH of 7.87, Githunguri cow dung digested slurry had a mean pH of 7.53, while Githunguri raw dung had a mean pH of 7.67 pH. The changes in slurry composition is due to biological processes such as conversion of organic matter into volatile materials methane and ammonia.

Electrical conductivity is the ability of aqueous medium to carry an electric current. The presence of dissolved solids such as sodium, potassium and magnesium in Bio slurry samples carry electric current through the liquid. The measured conductivity values showed there was presence of dissolved ions in the study samples. In this study conductivity values ranged from 13.03 mS/m for G3D to 22.40 mS/m for PGS3. PH and electrical conductivity tests have been shown to be good indicators of availability of ammonium nitrogen /total nitrogen and ions in aqueous solution. TDS values ranged between 7110 ppm for G3D to 16242 ppm for PGS1. Pig waste slurry had the highest electrical conductivity and total dissolved solids, which could be attributed to the presence of nutrients (for example, ammonium), the use of dietary salts, and in some instances groundwater containing salts. (Huang *et al., 2017*; Racz and Fitzgerald, 2001).

A great variation in physicochemical parameters and nutrient contents were observed in the analysed samples. This can be attributed to the difference in feeds, use of wash water and slurry age at the time of sampling. Slightly basic pH of manure can raise the pH of acidic soil upon prolonged application (Whalen *et al*., 2000).

Table 2: Macronutrient levels (mg/L) from slurry filtrate compared to inorganic fertilizer

Sample	N	P	Na	Mg	K
CDS1	19.80±0.45	57.64±0.62	49.19±5.42	0.37±0.08	91.00±1.00
CDS2	15.80±0.15	62.42±1.95	108.14±5.04	0.66±0.23	67.23±0.04
CDS3	12.40±0.83	110.59±0.50	49.47±1.99	0.42±0.11	71.63±0.10
PGS1	14.53±0.32	210.59±4.09	267.03±0.00	0.86±0.00	123.00±0.00
PGS2	11.30±0.42	255.09±0.70	268.03±0.00	0.96±0.00	145.00±0.00
PGS3	10.90±0.86	260.89±1.13	337.03±0.00	0.88±0.00	116.00±0.00
CHS1	12.40±0.23	187.08±2.19	155.76±4.10	0.43±0.06	197.67±1.33
CHS2	11.20±0.12	70.69±0.31	100.11±5.69	0.78±0.06	89.00±0.10
CHS3	10.80±0.38	203.71±1.07	179.38±3.33	1.59±0.33	91.33±0.59
G1D	13.40±0.25	147.37±2.57	4.26±0.84	0.81±0.04	121.29±1.96
G1R	16.60±0.21	174.96±1.93	16.15±8.24	0.43±0.18	306.17±0.16
G2D	11.70±0.14	108.54±3.78	45.33±2.07	0.41±0.08	139.73±0.46
G2R	12.40±0.24	163.31±6.33	44.49±5.52	0.41±0.12	208.00±1.40
G3D	14.70±0.39	146.88±0.78	27.28±0.99	0.21±0.01	12.76±0.00
G3R	16.40±0.43	107.13±4.58	63.73±3.31	0.20±0.04	20.76±00
UREA	468.00±0.13	62.79±0.16	40.10±6.42	0.18±0.05	0.00±0.00
NPK	173.40±0.19	584.31±0.03	14.35±0.92	0.00±0.00	25.24±0.00
CAN	274.50±0.12	7.56±0.01	7.90±0.08	0.64±0.02	0.00±0.00
DAP	189.80±0.12	818.33±0.06	99.13±6.14	0.78±0.03	0.00±0.00

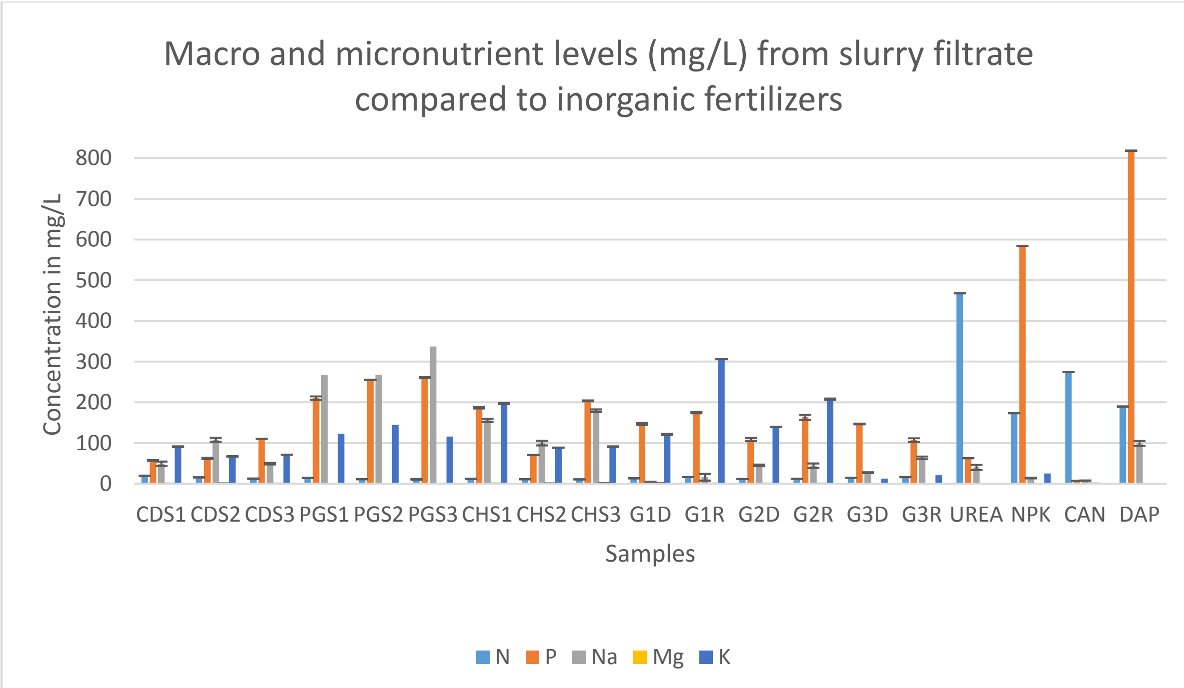

Figure 2: Macronutrient levels (mg/L) from slurry filtrate compared to inorganic fertilizer

Discussions of Results

Based on the ratios of NPK fertilizers can be classified into two: planting or sowing and topdressing. Two commercial fertilizers from the two categories were analysed for the levels of macro and micronutrients and compared to level in bio slurry samples. Fertilizers rich in phosphorous are applied during planting while those rich in nitrogen are used at different stages during the plant growth. All the commercial fertilizers had significantly higher levels of nitrogen.

Levels of nutrients in organic fertilizers vary depending on the sources of feedstock. The pig slurry had the highest levels of minerals. Pig waste had higher levels of total phosphorous (210.60± 4.10 - 260.89±1.10 mg/L) compared to chicken litter (197.10±2.20 - 203.70±1.10 mg/L) and cow dung feedstock (57.64±0.60 - 110.59±0.50 mg/L). Chicken manures commonly have higher contents of N, P, K and Ca (Carmo *et al., 2016*). Phosphorous levels increased with the retention time in the digesters. The levels of phosphorous in the slurry samples was lower than in planting fertilizer DAP (818.33±0.60 mg/L) and in NPK (584.30±0.20 mg/L).

Bio slurry had higher content of potassium compared to commercial fertilizers cow dung (67.20±0.03 - 306.20±0.16 mg/L). Levels of sodium were highest in DAP followed by the pig slurry. Sodium ions are important in soils due to salinity.

Pig waste slurry can serve better as a planting fertilizer due to its high P content while Cow dung slurry would best serve as a top dresser due to the high nitrogen content.

CONCLUSION

This study indicates that pig and chicken bio slurry tend to have high electrical conductivity and total dissolved solids. This could be attributed to the presence of nutrients (for example, ammonium), the use of dietary salts, and in some instances groundwater containing salts. Moreover the slurry samples had slightly basic P^H. Due to this they and can be used to raise the pH of acidic soil upon prolonged application. In addition, pig waste slurry can serve better as a planting fertilizer due to its high P content while Cow dung slurry would best serve as a top dresser due to the high nitrogen content.

REFERENCES

Arthurson, V. (2009). Closing the Global Energy and Nutrient Cycles through Application of Biogas Residue to Agricultural Land– Potential Benefits and Drawbacks. *Energies*, (2), 226–242.

Borges, D. L., Dias, L. F., da Veiga, M. A., & Curtius, A. J. (2003). Determination of cadmium in sediments and in sewage sludge by slurry sampling electrothermal atomic absorption spectrometry using iridium as permanent modifier. *Journal of the Brazilian Chemical Society*, *14*(2), 291-296.

Carmo, D. L. D., Lima, L. B. D., & Silva, C. A. (2016). Soil fertility and electrical conductivity affected by organic waste rates and nutrient inputs. *Revista Brasileira de Ciência do Solo*, *40*.

Groot, L., Bogdanski, A., & Bogdansk, A. (2013). *A review of scientific literature on the co-product of biogas production* (No. 55). Rome.

Huang, J., Yu, Z., Gao, H., Yan, X., Chang, J., Wang, C., ... & Zhang, L. (2017). Chemical structures and characteristics of animal manures and composts during composting and assessment of maturity indices. *PloS one*, *12*(6), e0178110.

Njogu, P., Kinyua, R., Muthoni, P., & Nemoto, Y. (2015). Biogas production using water hyacinth (Eicchornia crassipes) for electricity generation in Kenya. *Energy and Power Engineering*, *7*(05), 209.

Mugwe, J., Mugendi, D., Odee, D., & Mairura, F. (2009). Effect of selected organic materials and inorganic fertilizer on the soil fertility of a Humic Nitisol in the central highlands of Kenya. *Soil Use and Management*, *25*(December), 434–440. http://doi.org/10.1111/j.1475-2743.2009.00244.x

USEPA. (2010). Greenhouse Gas Emissions Estimation Methodologies for Biogenic Emissions from Selected Source Categories : Solid Waste Disposal Wastewater Treatment Ethanol Fermentation, (0210426).

Pratt, P. F. (1965). Potassium. *Methods of soil analysis. Part 2. Chemical and microbiological properties*, (methodsofsoilanb), 1022-1030.

Racz, G. J., & Fitzgerald, M. M. (2001). Nutrient and heavy metal contents of hog manure: Effect on soil quality and productivity. *Livestock Options for the Future*.

Warnars, L., & Oppenoorth, H. (2014). *Bioslurry a Supreme Fertilizer: A study on bioslurry results and uses*. (K. Atkinson, Ed.). Hague, Netherlands: Hivo People Unlimited, FSC.

Whalen, J. K., Chang, C., Clayton, G. W., & Carefoot, J. P. (2000). Cattle manure amendments can increase the pH of acid soils. *Soil Science Society of America Journal*, *64*(3), 962-966.